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INSTITUTE FOR DIRECT ENERGY CONVERSION

UNIVERSITY OF PENNSYLVANIA U., Philadelpia

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TOWNE SCHOOL OF CIVIL AND MECHANICAL ENGINEERING

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CONTENTS

APPENDIX

Detailed Progress Reports and Future Plans

Section 1

Summary of Technical Work

This section is a synopsis of the technical work in progress at the Institute. Detailed reports are included in the Appendix.

1. Biochemical Fuel Cell

Principal Investigator	-	Dr. J. O'M Bockris
Research Associates	-	Dr. E. Gileadi Dr. R. Bartha
Research Student	-	R. Blasco

The first phase of this investigation has been completed, and the results are presented as Appendix A of this report.

The primary aim of this first phase was to obtain answers to the following questions.

1. What is the order of magnitude of power densities attainable in biochemical systems?
2. What is the longevity of resting cell preparations?
3. Do enzymes play a direct part in the electron transfer process at the electrode?
4. What is the effect of the presence of organic matter at the electrode?

A "model" system was chosen to obtain the answers. This system was the decomposition of formic dehydrogenlyase. This enzyme was obtained from E. Coli which were grown under anaerobic conditions.

The study of the "model" system supplied the following answers.

1. The rate of hydrogen production was such as to allow power densities of 2-3 milliwatts/cm^3.

2. The enzyme system becomes deactivated slowly over a period of 11 hours.

3. Direct charge transfer from enzyme or the enzyme substrate complex could not be detected. This implies that this system is not a "direct" biochemical fuel cell.

4. The electrode does not become poisoned by the presence of the organic materials used.

The above study has suggested a logical second phase of the work.

Further work will be concerned with a system which may have practical importance, namely the enzymatic decomposition of glucose. This compound forms the end product of the hydrolysis of two very common and important material products, starch and cellulose.

It is intended to isolate and study the single steps involved in the fermentation of cellulose which is known to be a highly complex reaction which involves many steps and enzyme systems.

It is planned to use growing cell preparations or pure enzymes to develop means for long term continuous operation.

Details of the future work are part of Appendix A.

2. Plasma Physics - MHD

Principal Investigator	-	Dr. H. Yeh
Senior Research Associate	-	Dr. C. Gottschlich
Research Student	-	T. K. Chu

The ultimate aim of this investigation was:

1. To obtain a quantitative understanding of the phenomenon of non-equilibrium ionization.
2. To augment "industrial" investigations which are concerned with "bulk" or average effects, with detail measurements of local electron and ion temperature.

The program which has evolved consists of the following.

1. A potassium seeded argon plasma has been selected for study.
2. Electron temperature measurements will be made by spectrophotometric methods.
3. Ion temperature will be obtained by using a technique which has been used in combustion studies, but which has not yet been attempted in this area, namely the measurement of the "rotational" temperature of tracers of OH and CH radicals.
4. The measurement of "local" plasma conductivities by the use of potentiometric techniques.

The equipment has been installed. The quartz test section is in the final stages of assembly.

Theoretical calculations are in progress to predict the thermodynamic properties of the argon-potassium plasma. This is needed for the interpretation of the radiation intensity measurements.

Details are presented in Appendix B.

3. <u>Plasma Physics - Thermionics</u>

Principal Investigators - Dr. G. Schrenk
- Dr. L. Zelby

Research Student - Michael Kaplit

(3a)
A thorough study of the literature is in progress, which aims towards the end of:

1. Identifying the various "MODELS" which theoreticians have postulated.

2. To identify the basic assumptions and limitations of the above.

3. To attempt to reconcile these, if possible, or to identify their common elements.

4. To conceive, if possible, of a "general" model system which might include the above as special cases.

5. To isolate specific research problems based on the results predicted from the above.

The first results of this study are presented in Appendix C.

(3b)
A successful "model" has been developed for the analysis of plasma thermionic converters in the "passive" mode of operation.

This analysis has led to several important results.

1. Good agreement with experimental results was obtained.

2. The point of transition from "passive" to the "arc" mode of operation has been successfully predicted.

3. The analysis leads to the conclusion that the work function of the emitter must be a variable. These results suggest that it is necessary to study mechanisms which would produce such a variable work function.

Details are presented in Appendix D.

4. <u>Thermionics - General</u>

Principal Investigator - Dr. L. Zelby

During this period, work has been accomplished in three areas:

1. potential distribution between inclined planes initiated before (see Progress Report No. 1, 15 November 1962)

2. literature search and analysis regarding hollow emitters (see Status Report, October, 1963)

3. plans for future investigation in the area of thermionic emitters.

The first two items have been pursued in an effort first, to resolve the discrepancies in the reported analyses and experimental results; and secondly, to obtain a better understanding of the effects of electrode geometry on emission characteristics of emitters and the space charge potential distribution between the emitters. The third has been pursued in order to assess the present state of art and to propose a study in areas in which investigations would be most fruitful and would lead to a significant advance of the state of art.

Details are reported in Appendix E.

5. Thermal Energy Storage

(5a) Materials Synthesis - Thermo Physical Properties

Principal Investigator - Dr. G. Belton

Senior Research Associate - Dr. R. A. Sharma

Research Student - K. Rao

The aim of this program is as follows.

1. The selection of promising materials with melting points spanning the temperature range of $600^{o}C$ to $2,000^{o}C$.

2. The determination of needed phase diagrams, i.e. melting points of eutectic mixtures.

3. The determination of heats of fusion.

4. The determination of volume changes with phase change.

The status of this program is as follows.

A high precision Differential Thermal Analyzer has been built, and is in operation. It is capable of determining phase diagrams with high precision.

A precision "Dropping Calorimeter" has been built, and is in the final stages of assembly.

A galvanic cell apparatus is being built to enable the determination of partial molar properties of compounds.

The apparatus for the determination of volume changes is still in the design stage.

Details are reported in Appendix F.

(5b) Thermal Transport Studies

Principal Investigator - Dr. M. Altman

Research Students - H. Chang
D. Ross

The aims of this investigation are:

1. To obtain measurements of "effective" conductivities of thermal storage materials.

2. To obtain an understanding of the different contributions to the transfer of heat energy by radiation through the materials and the "normal" mode of heat conduction.

3. To develop analytical methods of predicting heat transfer through partially translucent materials.

The status of this program is as follows.

A review of the literature and our oven analyses have resulted in the selection of an experimental procedure for the determination of "effective" conductivities.

Details are presented in Appendix G.

The vacuum equipment has been installed and checked. Vacua of 10^{-9} torr are being obtained.

The test section for the determination of conductivities is still in the design stage.

Theoretical studies of phonon and photon heat transmission through solids and liquids are in progress.

The analytical methods which we published (A.I.Ch.E. Reprint No. 56, National Heat Transfer Conference 1963) have received considerable attention, as evidenced by the number of requests for reprints.

This work has stimulated analysis of the general problem of space power systems which utilize thermal energy storage. The analysis which was made, and the conclusions thereof were presented at NASA-Lewis. A copy of this presentation constitutes Appendix H. This appendix includes Dr. Schrenk's discussion.

6. <u>Solar Reflectors - Heat Receivers</u>

Principal Investigator - Dr. G. Schrenk

This work is a continuation of a study which Dr. Schrenk initiated before joining the Institute. Because of the importance of this work it was decided to enable the investigator to continue his studies under the auspices of this organization.

The aims of this study are.

1. To develop a mathematical technique which makes it possible to analyze solar collectors in a realistic fashion.
2. To determine the validity of a variety of assumptions which are commonly made in solar collector-heat receiver analyses, such as the use of a "Lambertian" distribution of energy flux from the cavity opening.
3. To analyze the systems aspects of collector-heat receiver-converter assemblies.

The results of this study have shown that the use of Lambert's law leads to flux distributions inside a cavity which are significantly different from the correct ones. This could lead to poor cavity designs which may not be able to allow for the actual heat distribution.

Details of this work are presented in Appendix I. The appendix also includes our future plans for a continuation of this effort.

Future work will be directed towards the inclusion of the effects of blockage of radiation by the structure of the heat receiver, and varying cavity openings.

Section II

Budget

INSTITUTE FOR DIRECT ENERGY CONVERSION

FINANCIAL STATEMENT

JANUARY 31, 1964

I

EXPENDITURES TO DATE		
CURRENT EXPENSE		
Major Apparatus	36,793.25	
Consumables and Minor Apparatus	10,714.46	
Machine Shop Labor, Installation of Equipment	12,060.90	
Employee Benefits	3,518.35	
Travel	1,921.07	
Miscellaneous	11,201.25	
TOTAL CURRENT EXPENSE		76,209.28
SALARIES		
Academic	37,307.58	
Administrative and Clerical	12,961.16	
TOTAL SALARIES		50,268.74
TOTAL EXPENDITURES, JUNE 30, 1963 THROUGH JANUARY 31, 1964		$126,478.02

PROJECTED EXPENDITURES

vs

FUNDING

February 1, 1964 - May 31, 1964

II

TOTAL FUNDING AVAILABLE FOR FY 1963-64 less University overhead charges. This amount is the sum of new money from NASA for 1963-64 and uncommitted funds from FY 1962-63	157,540.19	
EXPENDITURES through January 31,1964 See Page 12	126,478.02	
BALANCE		31,062.17
Average monthly operating cost to date for Salaries, Consumables, and Current Expense Items (this excludes University overhead charges and expenditures for Major Apparatus)	9,153.35	
Times 4 - (Feb., Mar., Apr., May) Equals Projected Cost to May 31, 1964		36,613.40
Excess of Projected Cost Over Funds Allocated for FY 1963-64		5,551.23

Section 3

Related Activities

In view of the fact that the primary function of the Institute is an educational one, it is appropriate to discuss our activities in that area.

The number of Ph.D. candidates who are engaged in thesis work in the area of energy conversion is now six. The number of post-doctoral researchers is three. Seven faculty members participate in our research and teaching activities.

We have developed a graduate course (1 yr.) in energy conversion which is attracting many students. Deliberations are currently in progress to expand this course into a new program of specialization.

Our work has led to several publications, some of which were reported in our last progress report.

Our last progress report should be consulted as to the standing of the Ph.D. candidates, and the expected completion of their doctorate program.

A number of invited papers is being prepared for the following meeting.

1.	Prof. H. Yeh	-	International Conference on MHD, Paris, 1964
2.	Prof. M. Altman	-	6th AGARD Conference on Energy Conversion, 1964
3.	Dr. G. Schrenk	-	6th AGARD Conference on Energy Conversion, 1964

Appendix A. Biochemical Fuel Cell

INTRODUCTION

The possibility of generation of electrical energy by the action of micro-organisms on organic matter was realized by Potter[1] in 1912, and the use of such systems as electrical half cells has later been discussed.[2] A half cell in which the electrode reaction is catalysed by a biological system present may be called a biochemical half cell and a fuel cell in which one or both half cells are "biochemical" will be termed a biochemical fuel cell (B.F.C.). Two types of B.F.C. should be considered[3]. The direct B.F.C., which converts the free energy released in the metabolic and growth processes of organism to electrical energy,* and the indirect B.F.C. which, in fact, acts as a biochemical fuel generator. The function of the latter type is to produce a fuel of high electrochemical reactivity from the reactant. It is essential for the understanding of the mechanism of B.F.C. reactions to distinguish between direct and indirect B.F.C. Direct experimental evidence showing that the formic acid-formic dehydrogenlyase systems studied here constitute an indirect B.F.C. electrode will be given below and some methods by which a distinction between direct and indirect B.F.C. can be made will be discussed.

Numerous examples of indirect B.F.C. have been reported. Among these are the decomposition of urea by urease[3] or by B. pasteurii[4] the production of ethyl alcohol by fermentation of glucose[5], the production of hydrogen by the action of Cl. butyricum on glucose[4] or by the action of E. coli on glucose[6] or on formic acid[7]. Direct B.F.C. systems are not common and, in fact, it is rather doubtful whether true direct B.F.C.'s have as yet been demonstrated to exist.

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*The detailed mechanism by which a direct B.F.C. will operate is not quite clear. One possibility would be that the enzyme-substrate complex formed in the course of the reaction will be adsorbed on the electrode and react directly with it.

In the present paper a short bacteriological and electrochemical study of the formic dehydrogenlyase enzyme system produced by E. coli grown under anaerobic conditions is reported. A very short experiment with the same enzyme system has recently been reported[7]. In the latter investigation cell extracts rather than whole cells were used and only a negative conclusion was reached, namely that the electrochemical activity of the substrate (formic acid) was greater than that of the product (H_2) under the experimental conditions chosen. As will be shown below (cf. Fig. 5) this is not the case when resting cell preparations are used.

EXPERIMENTAL

Resting cell preparations of Escherichia Coli ATCC 8739 were grown in deep culture on a medium consisting of 1% glucose, 0.2% yeast extract, 0.2% peptone, 0.8% nutrient broth, 1.4% Na_2HPO_4 and 1.4% KH_2PO_4. Conventional manometric techniques were employed to determine the formic dehydrogenlyase activity which is measured as the enzyme catalysed rate of hydrogen evolution from formic acid and expressed in terms of Q_{H_2}, the number of μ l. of hydrogen (S.T.P.)evolved per hour per mg. weight of dry bacteria. Manometric readings were taken at 10 minute intervals and the rate of hydrogen evolution (Q_{H_2}) was investigated as a function of time (up to six hours), concentration of substrate (formic acid 5 to 200 μ moles per cc.) and concentration of bacteria (0.75-7.5 mg./cc.). The cell preparation was suspended in a phosphate buffer of pH = 6.1 and thermostated at 37° C.[10]

Galvanostatic (constant current) current-potential relationships were obtained in a standard, three electrode, electrochemical cell at 37°C, with a normal calomel reference electrode. Bright and platinized Pt test electrodes (50 cm^2 geometrical area) were used as anodes with platinized Pt counter electrodes. Comparison runs with all components except the bacteria, with and without hydrogen bubbling through the cell were taken to evaluate the masking effect of the formic acid substrate - itself an electrochemically active substance - on the experimentally measured quantities.

RESULTS

Effect of Bacteria Concentration

The dependence of the initial rate of hydrogen evolution (Q_{H_2}) on formate concentration is shown in Fig. 1. The concentration of bacteria was kept constant at 1.5 mg (dry weight) per cc. A flat maximum (of $Q_{H_2} = 250\ \mu$ 1. $mg^{-1}\ h^{-1}$) is observed in the range of about 50 - 100 μ mole/cc and further experiments were thus conducted with a substrate concentration of 100 μ mole/cc.

Effect of Bacteria Concentration

In Fig. 2 the specific activity (Q_{H_2}) of formic dehydrogenlyase is plotted vs. its concentration in solution, at a constant substrate concentration (100 μ 1/cc). Highest Q_{H_2} values were obtained at a concentration of 1.5 - 3.0 mg bacteria (dry weight) per cc. of solution. The same data are shown in a different way in Fig. 3 where the volume of hydrogen V_{H_2} evolved per hour per cc of solution is given as a function of bacteria concentration. V_{H_2} increases monotonically with increasing concentration of bacteria but a tendency for it to level off is clearly indicated.

Time Effects

A decrease in Q_{H_2}, the rate of hydrogen evolution, with time was observed in all measurements.

In Fig. 4 the variation of Q_{H_2} with time is shown in two experiments where the initial formate concentration was 100 μ 1. cc^{-1}. Curve I was obtained at practically constant formate concentration (achieved by adding the calculated amount of formate solution every half hour with a microsyringe through self sealing serum bottle stoppers). The results of a comparison test in which no substrate was added during the experiment are shown by curve II in Fig. 4. About 70% of the substrate was used up by the end of this experiment. When the system was left overnight the activity decreased practically to zero and did not increase upon addition of substrate.

Current-Potential Relationship

Electrical measurements were taken in a standard three compartment cell, water jacketed to allow thermostating. The steady-state current-potential relationship was determined galvanostatically (i.e. by external control of the current) at successively increasing and decreasing current density. A normal calomel electrode was used as reference electrode and a platinized Pt counter electrode was used for polarization. Fig. 5 shows the V-i relationship for a 50 cm^2 platinized Pt electrode. Curves II and III were obtained in the same solution before the bacteria was added with and without hydrogen bubbling throughout the solution, respectively. Curve I was obtained in the presence of a large amount of bacteria.* In Fig. 6 a comparison between the behavior of bright and platinized platinum is shown. For both types of electrodes the rate of oxidation of hydrogen produced by the bacteria is compared to the rate of oxidation of hydrogen bubbled through the solution in the absence of bacteria.

DISCUSSION

Formic dehydrogenlyase is an inducible enzyme system formed by *E. coli* grown under anaerobic conditions. A resting cell preparation was used in this study, since it affords greater simplicity and better control of enxyme concentration (compared e. g. to growing cell preparations or to cell extracts). On the other hand, this puts rather severe limitations on the duration of each experiment, and a study of time effect was required before meaningful electrochemical data could be obtained.

Optimum concentrations of enzyme and substrate were determined, beyond which the specific activity tends to decrease, probably due to the inhibitory effect to excess substrate and to "overpopulation" at higher bacteria concentrations (Fig. 1, 2). Low Q_{H_2} values at the lowest formate concentration (Fig. 1) could be artificial and arise due to an appreciable change in substrate concentration before the first manometric reading (10 minutes). It is also possible, however, that in this range the rate of reaction is first order in substrate concentration. The inhibitory effect of excess substrate depends apparently not only on its absolute concentration in solution but also on the ratio of substrate to enzyme concentration, thus giving rise to lower specific activity of the enzyme at the lowest concentration measured (cf. Fig. 2).

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*An excessive amount of bacteria (3 gm) was used in this experiment so that the total amount of H_2 evolved would far exceed the amount which could be oxidized anodically on the electrode. In this way complications due to shortage of H_2 supply were avoided.

The observed decrease in specific activity with time is seen to be largely due to gradual inactivation of the enzyme system, and only a small part of it can be accounted for by the decrease in substrate concentration (Fig. 4).

The current-potential relationships observed experimentally (Fig.5) in the presence of bacteria are practically identical with those obtained with pure hydrogen bubbled in the solution. From this we may conclude that (a) the formic dehydrogenlyase-formate system represents an indirect B.F.C. anode in that it produces a fuel (H_2) which then appears to be oxidized in a conventional manner and (b) that the bacteria do not poison the electrode and thus do not interfere with the electrochemical oxidation of hydrogen upon it. A comparison of the current-potential behavior first on bright and platinized Pt in the presence of the micro-organism and then in its absence (but with the fuel produced by the micro-organism, in this case hydrogen, introduced into the system) is perhaps the best way to distinguish between direct and indirect fuel cells. Thus, while the rate of oxidation of fuel may happen to be close to the rate of charge transfer from the enzyme-substrate complex to the electrode, say, on a particular electrode material, these rates will be affected differently by a change in the properties of the electrode, and a clear distinction will be easy to make. In the system studied here the V-i relationship in the presence and absence of micro-organism was virtually the same on both bright and platinized Pt, showing that in both cases the reaction taking place is the anodic oxidation of H_2 in solution, independent of its origin. This is to be expected since most of the respiratory enzymes of bacteria are located in the cell membrane. The total distance from the cell membrane to the outside of the bacterial cell is approximately 200 Å[11], thus placing the enzyme substrate complex well outside the compact electrical double layer ($<$ 5 Å) and in a region of negligible electric field. Charge transfer from the enzyme substrate complex directly to the electrode (i.e. direct B.F.C.reaction) thus appears to be practically impossible as long as the active enzyme is surrounded by the cell wall.

It should be emphasized that the generation of electrical potentials associated with the introduction of micro-organism into a system does not in itself prove or even indicate the existence of a direct B.F.C. reaction. These potentials may well arise due to the formation of various degradation products in the vicinity of the electrode.

Estimated Power Density

A rate of hydrogen evolution of 1 - 2 cc per hour per ml. of solution can be maintained by this system for a period of several hours. The corresponding current would be 2.5 - 5.0 mA per cc of solution, assuming that all the hydrogen produced by the action of formic dehydrogenlyase on formic acid is oxidized anodically. Since the micro-organism does not seem to poison the electrochemical reaction, it is possible to construct a biochemical fuel cell using the present system as its bioanode, combined with a conventional (e.g. oxygen) cathode; which will operate at a potential of 0.6 - 0.8 volt at 37° C. Such a cell will have a power density of 2 - 3 mW/cc. Due to the low temperature required by the micro-organism it would only be possible to operate such cells at low current densities, unless the hydrogen generating part of the system is physically separated from the electrochemical converter.

CONCLUSIONS

Microbiological and electrochemical aspects of the system formic acid - formic dehydrogenlyase have been studied. Optimal enzyme and substrate concentrations have been determined and a slow deactivation of the enzyme system (over a period of six hours) has been observed.

The electrochemically active substance was shown to be the molecular hydrogen produced by the enzyme catalysed splitting of the formic acid substrate. Direct charge transfer from the enzyme or enzyme-substrate complex to the electrode could not be detected. A power density of 2 - 3 mW/cc can be maintained by this system at low current densities over 4 - 6 hours. To maintain the same level of hydrogen production over an extended period of time a dynamic (growing) cell preparation must be used and methods of closely controlling the rate of growth in such systems should be investigated.

FUTURE WORK ON BIOCHEMICAL FUEL CELLS

Introduction

The decomposition of formic acid by the formic dehydrogenlyase enzyme system found in E. Coli grown under anaerobic conditions was taken as a model reaction for the study of biochemical fuel cells. It enabled us to estimate the approximate power density attainable in such systems. The impracticality of using resting cell preparations for extended periods of time was clearly demonstrated and the effect of the presence of organic matter (the bacteria) on the electrochemical reaction at the electrode was shown to be negligible.

As a second step in this study a system of more obvious practical importance will be investigated, namely the enzymatic decomposition of glucose. This compound is perhaps the most important one to study for successful biochemical fuel cell operations since it forms the end product of the hydrolysis of two common and important natural products, starch and cellulose. In terms of use of waste materials, e. g. it is important to know that about 50% of the dry weight of human feces is composed of cellulose.

The fermentation of cellulose is a highly complex reaction, occurring in a great number of steps and involving many enzyme systems. A fundamental approach adopted here will be to isolate and study single steps in this reaction from both the electrochemical and biochemical points of view. Pure enzymes or dynamic, growing cell preparations of bacteria will be used to enable long term continuous operation.

Outline of Proposed Study

It is of major importance to determine unambiguously the overall reaction taking place during the degradation of glucose by any one enzyme system. In particular the overall reaction may depend on the applied potential and/or on electrode material.

A first step in elucidating the mechanism of the reaction would be to distinguish between steps occurring in the homogeneous phase and those which occur at the interface.

Considering specifically the steps which occur at the electrode, an attempt will be made to determine the effect of the electrode material, its mode of preparation, and to study the degree of coverage of the electrode by the bacteria or the enzyme, or by intermediates produced in the course of the reaction in each case.

Further, it is important to evaluate the rate determining step in the overall reaction and determine whether it is charge transfer dependent. Apart from a direct effect of the potential on the various steps in the overall reaction, the potential may affect the overall process indirectly e. g. by formation of an oxide layer on the electrode surface or by destruction of the enzyme or bacteria at some critical potential.

The central problem in the understanding of direct fuel cell operation is to evaluate the actual mechanism whereby the enzyme is effective in the charge transfer reaction. Thus the enzyme may have an effect of stabilizing the transition state, alternatively it may change the standard free energy of the reactants (in the rate determining step) or the products. A combination of the Hartridge constant flow method with current-potential measurements and with U. V. Spectroscopy may provide the answers to such questions.

It is of great interest to find out if the electrochemical activity observed in the presence of an organism is related to its essential life processes. Here ultrasonic radiation may be used in a flow system to burst the bacteria and a comparison of electrochemical activity before and after bursting could then be made.

Methods of lowering the energy of activation for the charge transfer process are of high technological and theoretical interest. Illuminating the system would be an obvious approach. In this respect it might be advantageous to stain specific parts of the cell and to illuminate these with a monochromatic light of a wavelength chosen for maximum absorption. It would thus be possible to introduce the light energy into the system at specific points. Alternatively, ionizing radiation could be used to the same end.

Live bacteria are generally known to carry a net electric charge in solution which is largely eliminated when the bacteria die, as is apparent from the enhanced rate of sedimentation under these conditions. It is both technically and theoretically important to ascertain the extent to which the existence of such net charges is associated with the metabolic activity of the micro-organism (e.g. could the charge be withdrawn by an electrode and then regenerated by the bacteria in solution).

Maintaining a dynamic, controlled-growth bacteria system is essential for long term operation of biochemical fuel cells of any kind. A study of the conditions required to maintain such systems will therefore be conducted, with special emphasis on control of the growth of the micro-organisms by regulation of the amounts of various essential trace elements.

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CAPTIONS TO FIGURES

Fig. 1 Initial rates of hydrogen evolution Q_{H_2} in μl. h^{-1} per mg of bacteria (dry weight) as a function of formate concentration.

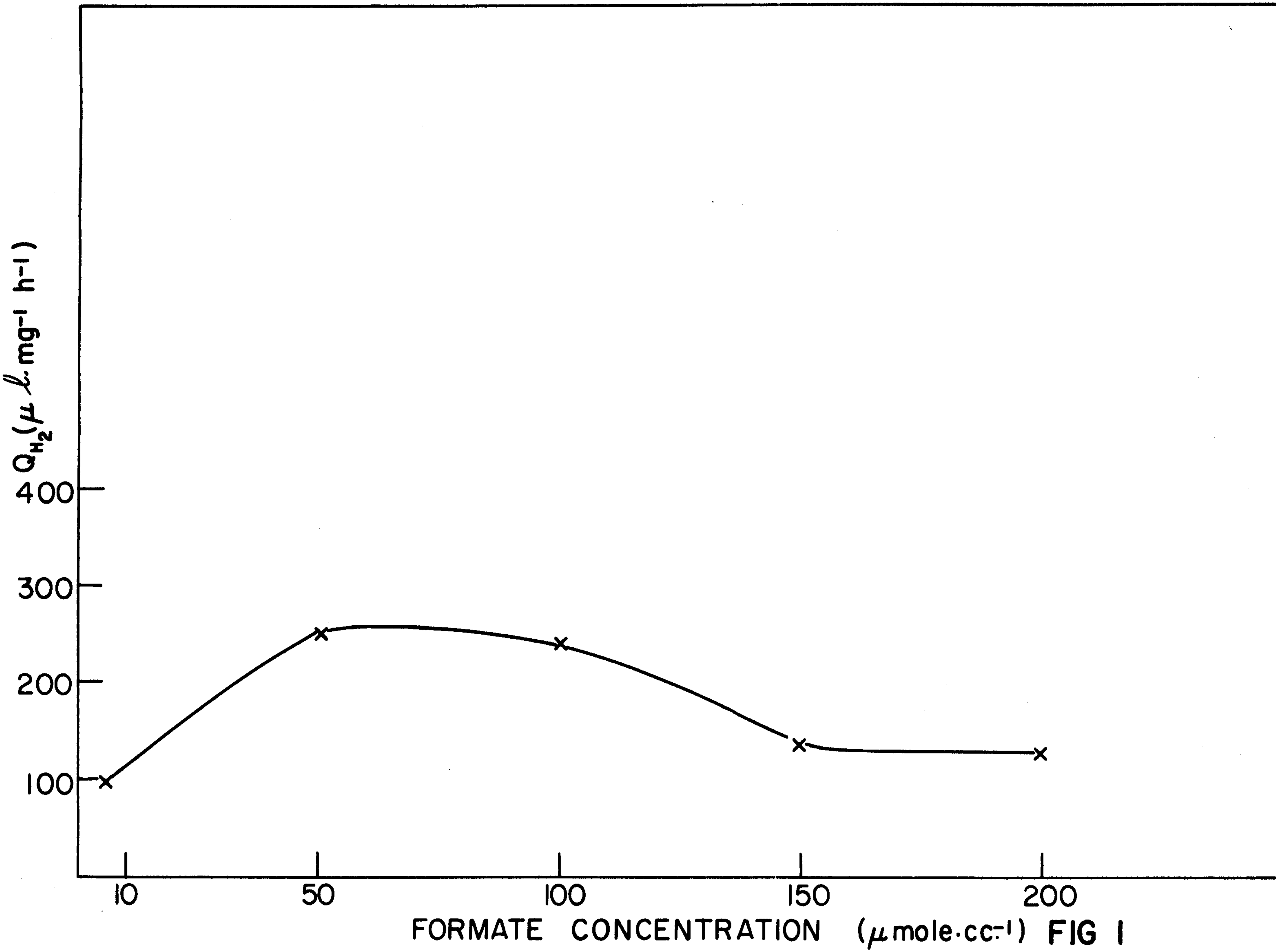
Fig. 2 Initial rates of hydrogen evolution Q_{H_2} as a function of bacteria concentration.

Fig. 3. Initial rates of hydrogen evolution V_{H_2} in μl. h^{-1} per cc. of solution as a function of bacteria concentration.

Fig. 4 The dependence of Q_{H_2} on time. Curve I: formate solution added every hour to keep concentration constant. Curve II: No addition of formate. (Initial formate concentration: 100 μ mole. cc^{-1}).

Fig. 5 Current-potential relationship for the formate-formic dehydrogenlyase system. Curve I: micro-organism and hydrogen absent. Curve II: micro-organism absent but hydrogen bubbled through solution. Curve III: Micro-organism added.

Fig. 6 A comparison of the current-potential behavior observed on bright and platinized Pt electrodes with the micro-organism present (△ △ △ ; 0 0 0) and with hydrogen bubbled through the solution (▽ ▽ ▽ ; □ □ □).



Q_{H_2} ($\mu \ell \cdot mg^{-1}\ h^{-1}$)
400
300
200
100
10
50
100
150
200
FORMATE CONCENTRATION (μ mole·cc^{-1})

FIG 1

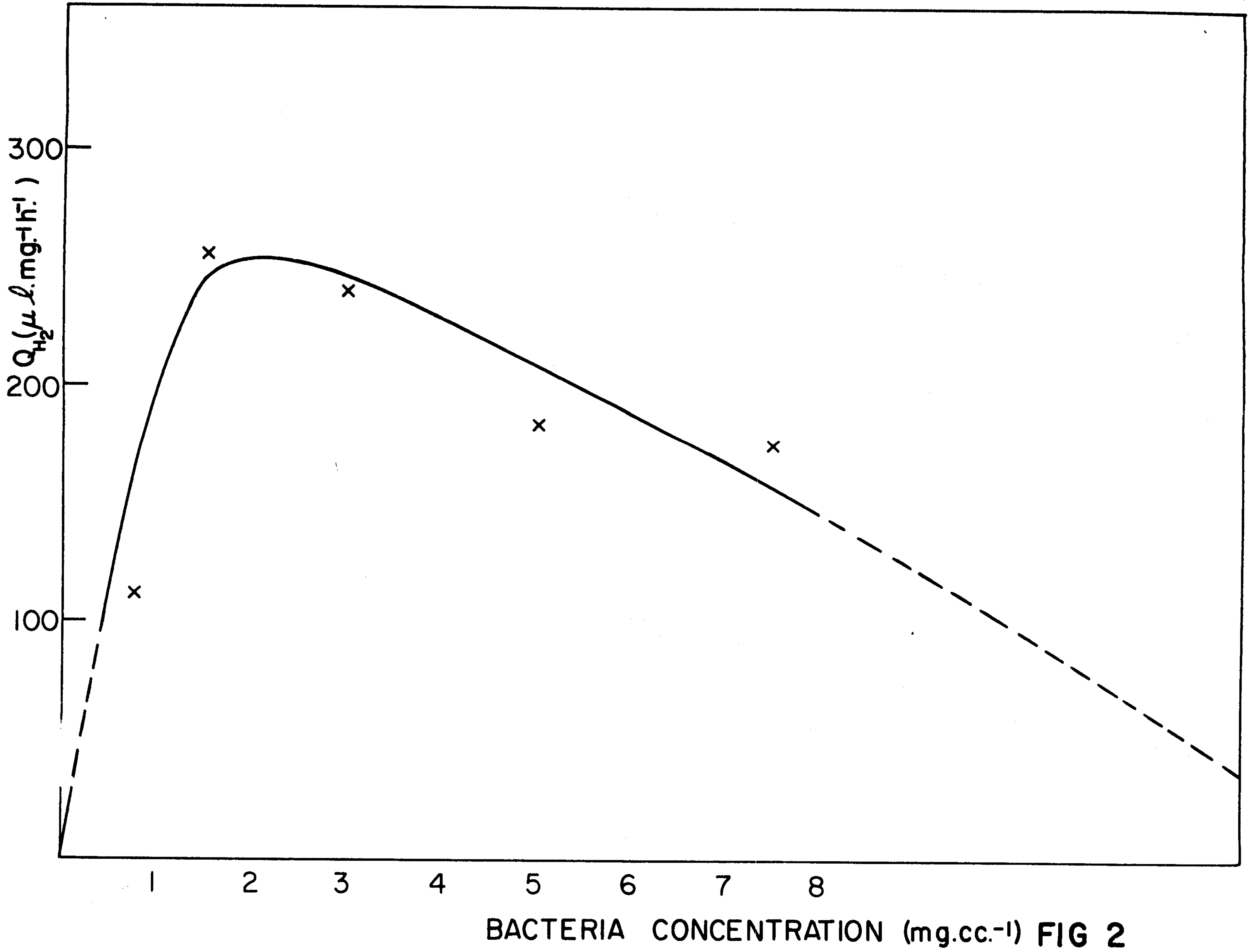
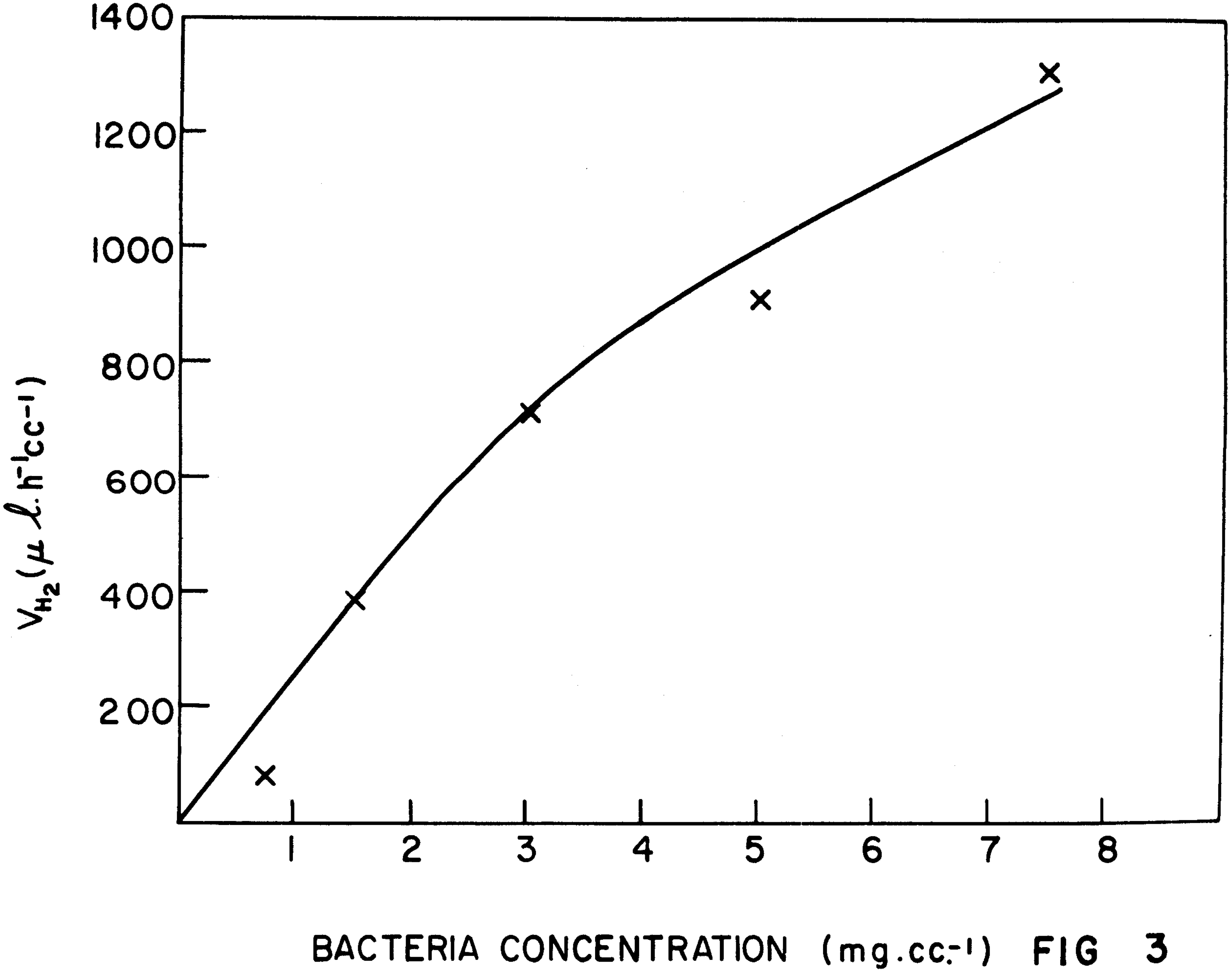

300
200
100
Q_{H_2} (μl.mg^{-1}h^{-1})
1
2
3
4
5
6
7
8
BACTERIA CONCENTRATION (mg.cc.$^{-1}$)

FIG 2



V_{H_2} ($\mu l.h^{-1}cc^{-1}$)
1400
1200
1000
800
600
400
200
1
2
3
4
5
6
7
8
BACTERIA CONCENTRATION (mg.cc.$^{-1}$)

FIG 3

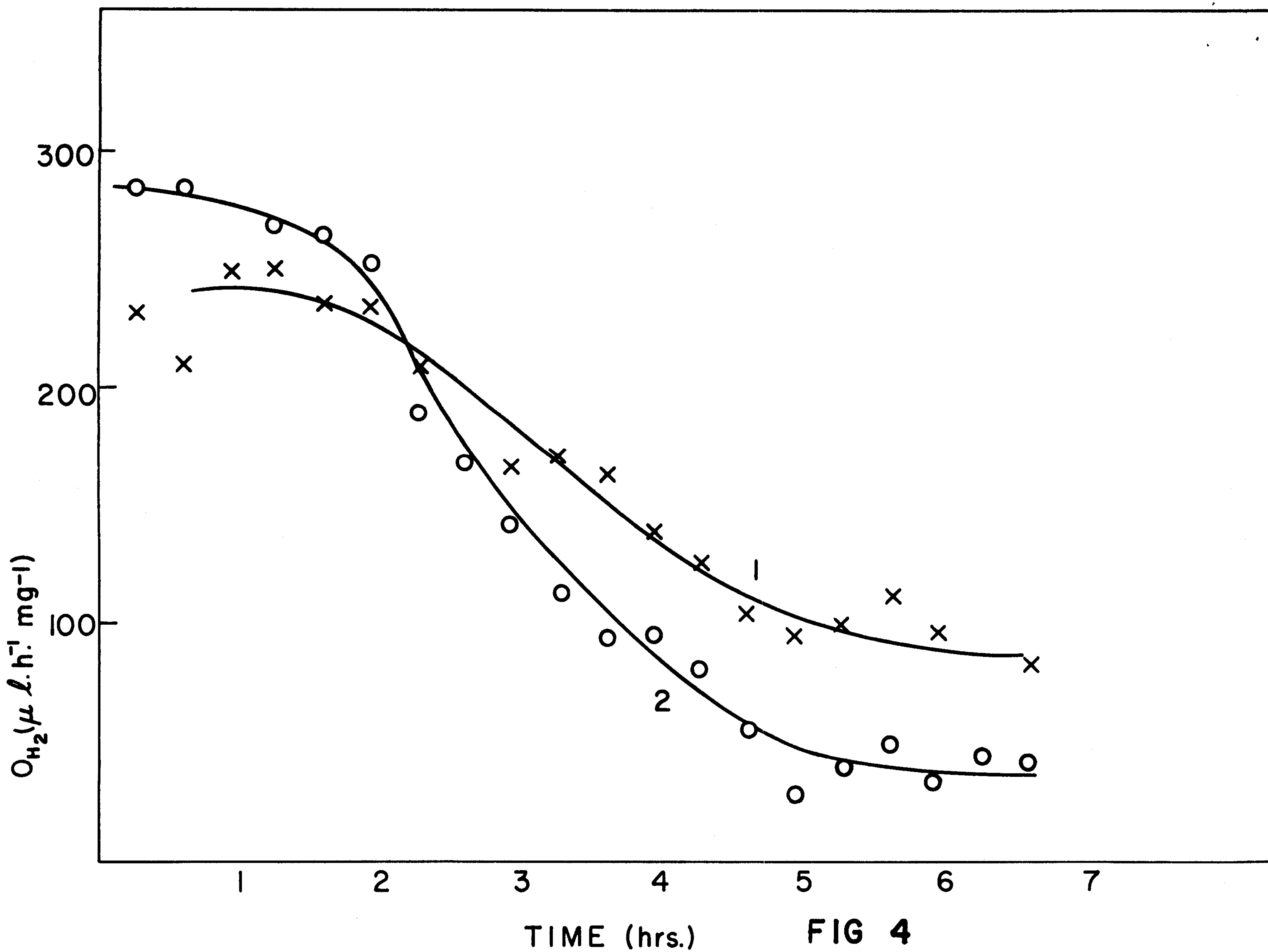
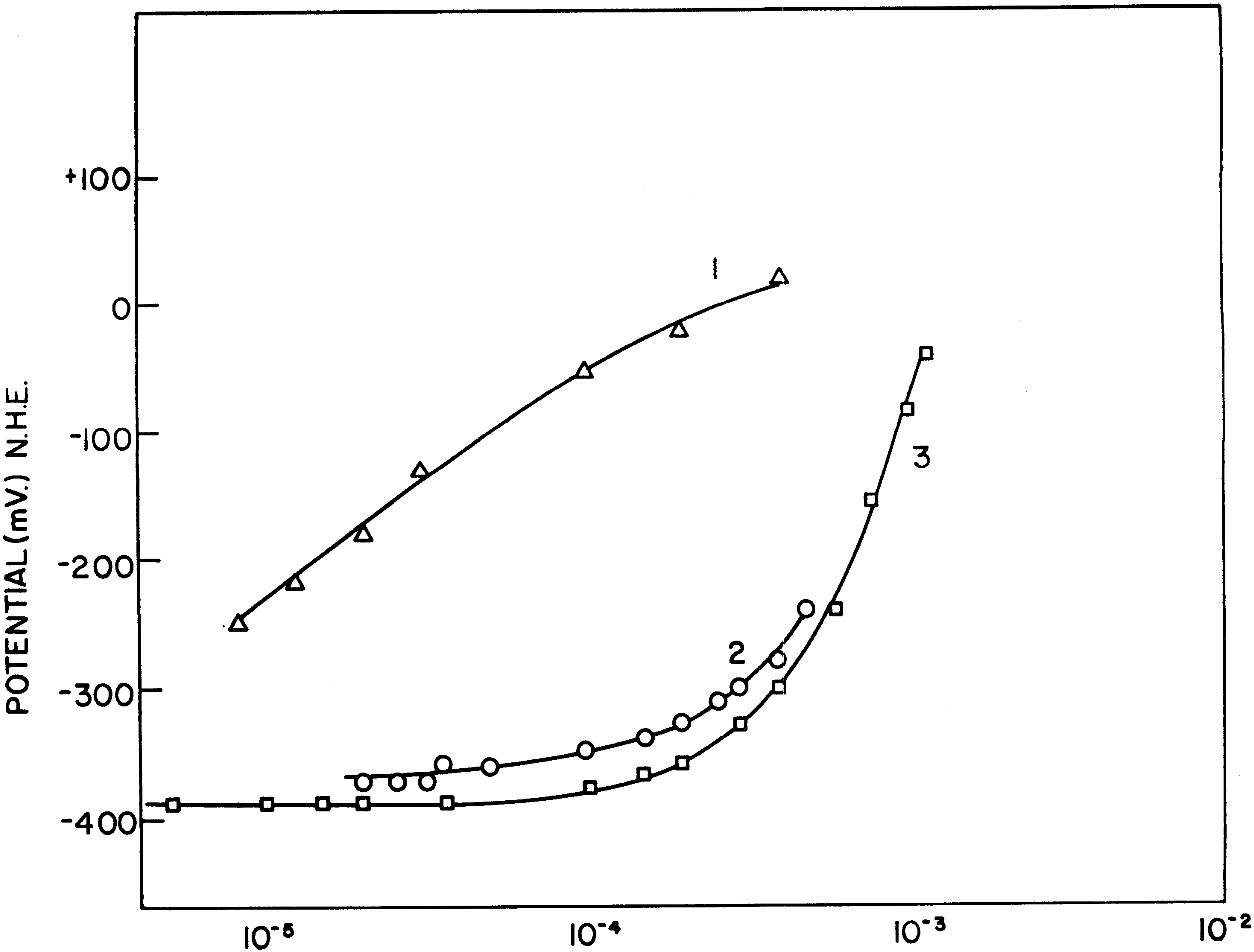


FIG 4



POTENTIAL (mV.) N.H.E.
+100
0
-100
-200
-300
-400
1
2
3
10^{-5}
10^{-4}
10^{-3}
10^{-2}
CURRENT DENSITY (A.cm⁻²)

FIG 5

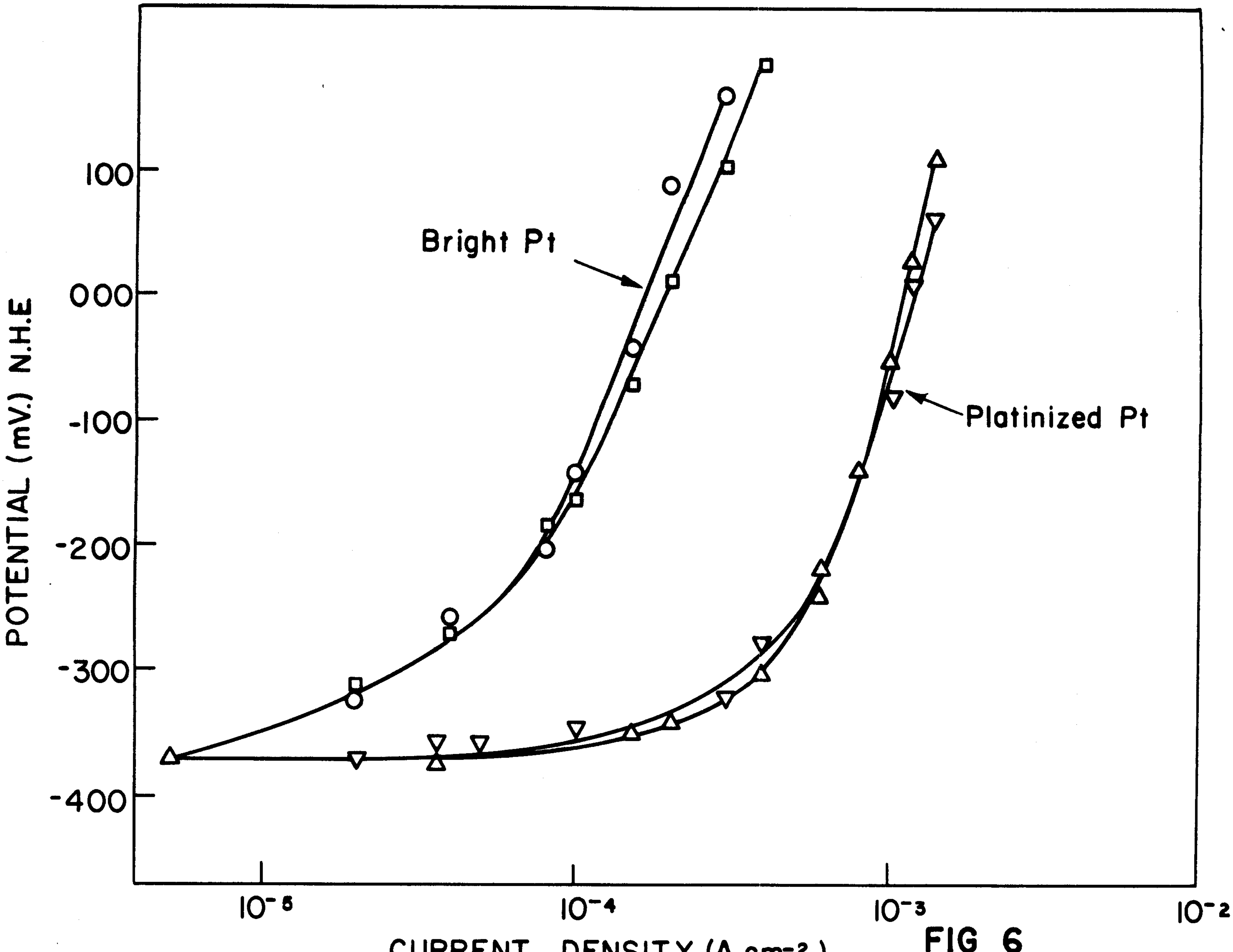

POTENTIAL (mV.) N.H.E
100
000
-100
-200
-300
-400
Bright Pt
Platinized Pt
10^{-5}
10^{-4}
10^{-3}
10^{-2}
CURRENT DENSITY (A.cm^{-2})

FIG 6

Appendix B. Plasma Physics - MHD

It has long been known that in a low-pressure gaseous discharge, the electron temperature is much higher than the atom and ion translational temperatures. This occurs because the electric field supporting the gaseous discharge supplies energy preferentially to the electrons. The atoms and ions are then raised in temperature by collision with the electrons. Because of the large difference in mass between an electron and an atom, only a small fraction of an electron's energy is transferred to an atom in an elastic collision. This results in a large difference between the electron and atom translational temperatures.

It is also well known that the electronic excitation and ionization cross sections for electron-atom collisions are much larger than for atom-atom collisions. Thus, if there is a large difference between electron and atom translational temperatures, the degree of ionization and level of electronic excitation of the atoms should correspond to the electron temperature rather than the atom temperature.

Kerrebrock(1) appears to be the first to have made use of these facts to produce an increased level of ionization, and thus an increased electrical conductivity, in a potassium-seeded argon plasma under conditions such as might be encountered in a magnetohydrodynamic power generator. Of course, this is not a low pressure plasma. The crucial factor, however, is a low electron density. The total pressure of the plasma does not play a first-order role.

The existing theory of an elevated electron temperature is quite simple and has been discussed by Kerrebrock(1) and Hurwitz et al (2) as well as by others. For a steady-state, spatially uniform plasma the electron temperature may be calculated from an energy balance in terms of the rate at which energy is delivered to the electrons and the rate at which the electrons transfer energy to the heavy particles by collisions. Under steady state conditions, the predicted temperature difference is

$$T_e - T_A = \frac{2}{3} \frac{M_A}{R\delta} \left(\frac{\sigma E}{en_e}\right)^2$$

where $\underline{T_e}$ is the electron temperature, $\underline{T_A}$ is the atom temperature, $\underline{M_A}$ is the molecular weight of the atoms, $\underline{R}$ is the universal gas constant, σ is the electrical conductivity, $\underline{E}$ is the electric field intensity, $\underline{e}$

is the electronic charge, n_e is the electron number density, and δ is a constant characteristic of the heavy particles. For electron collisions with atoms δ is about 2. For collisions with molecules δ is of the order of 10 to 1000.

The practical significance of non-equilibrium ionization is substantial because one of the major problems associated with MHD power generators is the high gas temperature required to produce an adequate electrical conductivity. Temperatures of the order of 3000°K are required which implies severe material problems. One answer is to cool the surfaces in contact with the hot gases. This produces a large heat loss, however, which limits the power generation efficiency of an MHD generator. Kerrebrock's work suggests one answer then, i.e., if we can make the electron temperature high while keeping the gas temperature low one obtains a high electrical conductivity at gas temperatures that can be tolerated by existing equipment.

Aside from refinements of the theory to account, for example, for spatial non-uniformities, the principal uncertainties are finding appropriate values for δ, σ, and n_e. Based on earlier remarks it is assumed that the electron density may be calculated from the Saha equation using the electron temperature. The uncertainty with respect to the Saha equation arises because it is derived on the basis of a system in equilibrium; but in this case it is being applied to a non-equilibrium plasma. In particular the radiation field is far from equilibrium because the plasma is small compared to the mean free path of the radiation. However, if collision induced transitions are more frequent than radiation transitions then one can ignore the non-equilibrium in the radiation field.

Based on calculations by McWhirter [(3)] the electron concentrations required to produce a collision dominated plasma is quite low, of the order of 10^{14} electrons per cubic centimeter. This is lower than the electron concentrations to be expected in an MHD generator. Thus it should be safe to use the Saha equation.

Some experimental work has been done (1, 4, 5) to observe the elevation of the electron temperature and the increase of electrical conductivity that results. But these measurements yielded only averages of the properties in a spatially non-uniform plasma. The results could only, then, be in qualitative, not quantitative, agreement with the theory.

Currently, related work is going on in several laboratories. Among these are the Valley Forge Laboratory of General Electric. Zauderer [6] has made a shock tube study of magnetically induced ionization. Shair, at the same laboratory, is developing a facility in which a noble gas will be heated by resistance heaters rather than by an arc. He has not yet obtained any measurements. Kerrebrock at M.I.T. is continuing his work on the problem. In each of these cases, as in the earlier published work, average values of properties over spatially non-uniform plasmas are being measured.

We wish to make more quantitative experiments on the elevation of the electron temperature and its effect on the ionization level and electrical conductivity. The basic idea of our experiment is to generate a high temperature (2000-3000°K) stream of argon seeded with potassium metal vapor. The potassium, because of its low ionization potential, is the source of electrons. The plasma will be observed as it flows through a quartz test section. Annular electrodes will be provided at each end of the test section. Together with an external D.C. power source they will produce a current and an enhanced electron temperature as discussed earlier. By observing the light emitted by electronic transitions in the atoms of the plasma, its electron temperature may be obtained by any of several well known methods (7, 8). The measurement of the translational temperature of the atoms constitutes a far more challenging problem. Several possibilities exist for doing this.

(1) The gas leaving the test section is cooled in a calorimeter. From the heat release the average gas temperature may be inferred. Corrections will have to be made for the non-equilibrium ionization but this should not be difficult. The difficulty is that only the average temperature of the gas at the test section exit can be measured.

(2) Thermocouples or probes of some kind can be inserted into the plasma. The difficulties are in making the proper radiation corrections, making corrections for the disturbances produced by probes in the stream, and finding materials that will survive the high gas temperature.

(3) Doppler broadening of line radiation that is not affected by collision and Stark broadening, e.g., lines produced by excited electrons in the unfilled internal shells of a transition element. Iron has

been used for this in the past by investigators in Germany and Russia. This requires extremely high spectral resolution, of the order of 1,000,000 or perhaps better because the gas temperature will only be about 2500°K.

(4) Perhaps the best possibility and the one that we shall try first is to spectrophotometrically measure the rotational temperature of some diatomic molecule such as the OH or CH radicals. This technique has been used incombustion studies. OH and CH are particularly desirable because the spacing of lines in the rotation-vibration band is wide enough to be easily resolved by spectrometers of moderate resolution. We can work only with traces of the molecule present, however, because the collision factor δ is much larger for molecules than for atoms and tends to suppress the enhancement of the electron temperatures.

Supplementary electrodes installed in the wall of the quartz tube will yield information on the electric field in the plasma. The voltage drop between these electrodes must be measured with a potentiometer to avoid a current flow that would introduce electrode voltage drops. These field measurements together with the total secondary current flow and the temperature distribution can be used to obtain the local values of the electrical conductivity in the plasma.

The above measurements constitute a sufficient set to make quantitative comparisons between the theory and experiments.

Nearly all the equipment required to make these measurements has been built. We have an 80 KW Thermal Dynamic plasma torch with power supply, cooling system and instrumentation. This will provide the high temperature argon stream. A dry box has been constructed which contains a motor driven hypodermic syringe. This will be used to meter potassium into a secondary argon stream. This stream is heated in a furnace to vaporize the argon and then mixed in a special mixing chamber with the high temperature argon from the plasma jet. All of this equipment has been completed and installed on our plasma jet facility. The quartz test section has been ordered and delivery has been promised for the middle of February.

A Jarrell-Ash 0.5 meter spectrophotometer has been purchased. It is chopper stabilized and has a photomultiplier detector. The output signal is amplified by a "lock-in" amplifier and recorded on a strip chart recorder. The radiation from the plasma is transferred to the spectrophotometer by a scanning device mounted on an optical bench. The spectrophotometer and all its accessories are now in our laboratory and assembled but have not yet been aligned and adjusted.

We are just starting the theoretical calculations of the thermodynamic properties of the argon-potassium plasma. These are necessary so that we can relate the radiation intensity to the temperature and composition of the plasma. The procedures for doing this are well known and have been described elsewhere (9, 10). It is clear that most of our work remains to be done as it is only now that the assembly of our equipment is nearing completion.

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Appendix C. Thermionics - Review of Theory

A large number of theoretical models has been analyzed in order to describe the operation of, and obtain design criteria for, a parallel plane plasma thermocouple. Various models have succeeded in accurately predicting various ranges of the experimental I-V curves, and have succeeded in qualitative justification of the transition region from the extinguished to the ignited mode. With a fairly large effort in this direction, we might be tempted to remark that there is a distinct possibility that no one theoretical model will be adequate to cover the entire range of I-V relations in a thermionic plasma converter.

Several recent models are briefly discussed below, and recommendation for areas of study are made.

A. Models

The models described here, all for infinite, parallel planes, differ among themselves in certain assumptions regarding the type of species within the interelectrode space, the potential distribution, or the relative importance of diffusion or field currents.

McIntyre's[1, 2] treatment includes the emission of electrons at the collector, and production of both ions and electrons at the emitter. He, then, solves Poisson's equation numerically for these conditions to obtain the potential distribution in the interelectrode region. A large number of curves is produced, with rates of emission as parameters. Reduction of these curves to I-V characteristics is, unfortunately, not available. Analysis of some of these potential curves seems to indicate, however, that this is not a particularly suitable model.

A more realistic model[3] includes both species, electrons and ions. The transport equation, in terms of the diffusion approximation, is solved for the two species being scattered by neutral molecules. The resulting charge density and potential distribution are similar to the state of equilibrium: the plasma is essentially neutral, the electric field very small, and diffusion currents predominate.

A still better model appears that of Leffert[4] who includes in his analysis the sheaths at the emitter and the collector. The ion density in the region between the sheath is assumed spatially uniform; and the ion loss rate, independent of the voltage. The general character of the I-V curves obtained from this model shows excellent agreement with the theory, i.e. the trends, and various regions of operation are clearly indicated. The quantitative agreement between this model and experimental results in surprisingly good in some regions. By fitting the theoretical curves to the data, good agreement is obtained over wide range of operation.

Another model, based on the analysis of the sheath at the emitter[5] leads to negative resistance regions of the plasma thermocouple, and shows good qualitative agreement with some experimental results.

More recent work of Hernqvist[6] considers the ball of fire mode (ignited) in the cesium converter, and assumes ionization via resonance. Furthermore, he assumes that trapping of resonance radiation leads to longer effective lifetime of excited states ($\sim 10^{-5}$ sec.). The resulting I-V curves show good agreement for $(I/I_{saturation}) < .35$.

Carabateas and Kniazzeh[7] also use radiation trapping and extended effective lifetime of excited states, in addition to some assumptions about collisions and diffusion, as well as sheaths at the electrodes. The results of their calculations compare very favorably with some experimental results.

Dunlop and Schrenk[8] assume a neutral plasma, and neglect the thickness of the sheaths at the electrodes. The results of this model agree quite well with an I-V curve in the extinguished mode, and predict accurately the transition to the ignited mode. The model does not, however, describe the ignited mode.

The models of Hansen and Warner[9] and Warner[10] include electron rich and ion rich sheaths, respectively, in their analysis of the extinguished mode. They, too, neglect the thickness of the sheaths, and obtain good agreement with experimental data.

B. Recommendations

Analysis of the models presented above indicates that in the extinguished mode, at least, the inclusion of sheaths at the collectors leads to a reasonably satisfactory model, even when the sheath thickness is assumed zero. In the ignited mode, radiation trapping and extension of the lifetime of the excited states seem to yield a satisfactory model. It appears reasonable, then, to consider two models for the two different regions of operation such that transitions from one mode of operation to another could be accurately predicted. It is possible that the effects of sheath thickness variation may be important in such predictions. With respect to prediction of I-V curves it is recommended, therefore, that in some of the above models the sheath thickness be included. Since the Hernqvist model shows very good agreement for low currents, the sheath might be added to his model.

Other areas of study include the effects of the geometry of the electrodes, temperature gradients, and emission and emissivity of the electrodes.

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Appendix D. Thermionics - Analysis of "Passive Mode"

During the past year a theoretical model of a cesium plasma diode has been formulated. This model applies to a plasma diode whenever a fully randomized plasma is formed in the interelectrode spacing in both ion rich and electron rich conditions. This model takes into account plasma resistivity, surface ionization, and volume ionization and recombination effects. A phenomenological macroscopic approach is used to formulate the set of 13 simultaneous equations that describe this model. These equations are solved on an IBM 7094 computer.

Several solutions have recently been obtained from this model and compared to experimental data. The voltage-current characteristics predicted agree favorably with experimental data in the passive mode of operation and in the prediction of the point where the arc mode starts. An outline of this model and initial comparisons with experimental data were presented and published in Reference 1.

This model is currently being used to study in detail the transition from the passive mode to the arc mode of operation of a plasma diode. The success of this model in predicting this transition point has been traced to a near exponential increase in the volume ionization rate near the transition point. In this model a single step ionization mechanism has been used; experimentally, however, the ionization mechanism is unknown. Thus, one raises the question of what possible effects other proposed ionization mechanisms would have on the prediction of this transition point. An investigation of this question will be carried out, as discussed in 2) below.

This model is also unable to calculate arc mode phenomena. This has been traced to the fact that the conservation equations used in this model say that it is impossible to draw a current appreciably greater than the saturated emission current predicted by the Richardson equation. Thus, the emitter work function must be allowed to vary from the value used in the passive mode calculations if this model is to predict the large currents observed in the arc mode. Thus, we are led naturally to the conclusion that we must study mechanisms by which the emitter work function can vary in order to predict arc mode operation within the framework of this model. One related aspect of this problem is presently being investigated at the Institute, namely, the prediction of emitter work functions of surfaces partially covered by Cesium in the presence of strong fields. Other aspects of this problem are discussed in 3) below.

With the completion of this initial model, emphasis is now being directed to the following:

1) A theoretical exploration of the various modes of operation of the plasma diode will be carried out with this model. Specifically, it is possible to use either a negative or a positive sheath for the emitter and the collector sheaths in this model. Various possible combinations of these sheaths should correspond to various modes of operation; thus, by specifying various sheaths, this model can be used to explore the transition regions between various modes. For example, we believe that the transition into the ignited mode corresponds to a transition from a negative to a positive emitter sheath. By looking at solutions for both negative and positive emitter sheaths near the transition point, this model will be used to study the transition point and its associated hysteresis effects.

Extensive correlations of these calculations will be made with experimental results available both in the published literature and from NASA-Lewis. It is anticipated that this work will lead to a better understanding and definition of the various modes of a plasma diode.

2) Various proposed ionization mechanisms will be studied and their possible effects on the predicted performance of the plasma diode will be calculated. For example, our successful prediction of the transition point to the arc mode has been attributed to a near exponential increase in the volume ionization rate. Now, our model assumed a single step ionization mechanism; thus, it is imperative that we examine the possible effects other proposed ionization mechanisms would have on the prediction of this transition point. Also, the prediction of other observable effects may also depend on the ionization mechanism, such as the presence or absence of certain possible modes, the hysteresis effects at the transition points between various modes, etc. It is anticipated that this work will lead to a better definition and understanding of effects that depend on the ionization mechanism. It may also give some insight in the question of what is the correct ionization mechanism.

3) Arc mode phenomena will be studied theoretically. As has been pointed out, the failure of our present model to predict arc mode operation has been traced to the fact that our model assumes that the emitter work function is a constant. Thus, this study will start by investigating ways in which the emitter work function can vary. This work, however, will not be limited to the framework of our present model. Other approaches to calculating arc phenomena will also be studied with the viewpoint that an entirely different approach may be required to predict arc mode performance. The goal of this work will be to predict arc mode operation quantitatively.

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Appendix E. Thermionics - General

Attempts to calculate the integral derived in the report of November 1962 have been continued (the integral sign and the differentials $dr_n d(r_n \theta)$ should be removed in equations 3-5). A result has been obtained for a constant radius r,

$$\phi = \left(\frac{9}{4\epsilon_0}\right)^{\frac{2}{3}} \left(\frac{M}{2e}\right)^{1/3} \left(J_0 r^2 \theta^2\right)^{2/3} \tag{1}$$

so that

$$J_0 = \frac{4}{9} \epsilon_0 \left(\frac{2e}{M}\right)^{1/2} \phi^{3/2} (r\theta)^{-2} \tag{2}$$

which is exactly analogous to the expression for current density between <u>parallel, plane</u> electrodes.

This result is quite different from that obtained by Meltzer

$$\phi = \left(\frac{M}{2e}\right)^{1/3} \left(\frac{J_0 r^2}{\epsilon_0}\right)^{2/3} \left(\sin \frac{3\theta}{2}\right)^{4/3} \tag{3}$$

which, intuitively, does not seem reasonable: the potential is zero for $\frac{3\theta}{2} = \pi$, i.e. $\theta = 2\pi/3 = 60^{\circ}$. Both derivations will be checked to determine this discrepancy, since the periodic solution (eq. 3) might exist in an ion neutralized electron flow.

<u>Hollow Emitters</u>

Continued literature search revealed even greater discrepancies in predicted and measured current densities than those reported before (October 1963). The greatest discrepancy exists between the work of Brunn[2] and that of Brodie and Niewold[3]. The former contends that in hollow spherical cathodes "larger emission currents than the equivalent parallel plane cathode" can be obtained at <u>all voltages;</u> and current densities of the "order of 30 amp/cm^2 are easily obtainable". In addition

Sandor[4] contends that a potential minimum of the order of several volts can be produced within the cavity. The latter (Brodie and Niewold) contend that in order for the hollow emitter to be "capable of delivering current densities required for thermionic energy converters...even under the most favorable conditions, the hole diameter would have to be less than 0.003 cm".

The usefulness of the hollow emitters as high current density sources has been recognized by workers concerned with electron beam devices, particularly in plasma-beam amplifiers[5] because of their favorable characteristics with regard to ion bombardment of the emitting surfaces. These high current density sources might be useful as an experimental vehicle in thermionics. If Brunn's[2] and Sandor's[4] conclusions are correct, a reasonably energetic beam (several ev) would be available without the use of external potential, which might aid in experimental studies of ionization mechanism, and low voltage arc initiation.

Proposed Study

To date, two essentially different models have been postulated to describe the two different modes of operation of the plasma diode: the passive mode (extinguished) and the ignited mode (arc). Aside from considerations of different interelectrode distances in terms of the electronic mean free path, the two basic differences in the models lie in the considerations of sheaths at the electrodes and surface ionization for the passive mode, and sheaths, radiation trapping and volume ionization for the ignited mode. There is no one model, however, which can describe with reasonable accuracy both modes of operation. Several of the better models, and their ranges of applicability, as well as suggested extensions will now be discussed.

Models

A. Passive Mode

The best model, by far, appears that of Leffert[6]. In addition to the inclusion of different combinations of positive (ion rich) and negative (electron rich) sheaths at the two electrodes, he assumed: a. neutrality of the interelectrode plasma; b. spatially uniform, but voltage and time dependent, electron and ion distribution throughout the plasma; c. Maxwellian velocity distribution for both species. The results, quite comprehensive, include I-V curves for various combinations of sheaths, as well as comparison of experimental and theoretical results. By fitting, via changes in various parameters, the agreement between the experimental and theoretical curves can be made excellent. The lack of accuracy in use of actual parameters is attributed to variations of effective electrode areas and ion loss rate with the applied voltage, non-zero resistivity of plasma, space charge phenomena in addition to those at the sheaths, volume recombination of ions, and patchy emitter surface. Inclusion of volume recombination, however, was shown to be of little consequence.

Talaat[7] treats both modes, and contends that both depend on the ratio of the electronic mean free path to the interelectrode spacing, identifying the passive mode with surface ionization, and ignited mode with volume ionization. A rather interesting conclusion is the requirement of very low (no figure is given, unfortunately) vapor pressures leading to substantial lowering of emitter work function and high output currents ($\sim$ 15-18 amp/cm^2). Relatively good agreement is obtained between experimental and theoretical results. This model does show a moderate fit for both modes of operation.

The positive and negative sheath were investigated quite accurately[8], under the assumption of low degree of ionization, negligible volume ionization and recombination, and the domination of diffusion effects except in the sheath. The results of the model cannot, at least at present, be verified experimentally. Furthermore, the calculation of the sheaths leads only to one point on the I-V curve. Consequently, for comparison with available experimental data, a large number of calculations would be required.

Hansen and Warner[9] and Warner[10] consider negative, and positive sheaths, respectively. The results of the study on negative sheaths[9] compare favorably with experimental results after discrepancy with respect to saturation currents has been removed. The study on positive sheaths[10] has not been compared with experiment, but conclusions appear in accord with those of Blue et al[8], i.e. that, in the case of positive sheaths here, diffusion is important in the passive mode.

Finally, Dunlop and Schrenk[11] use a model, which appears to be a refinement of that of Talaat[7], which includes volume ionization and recombination. This model leads to excellent agreement between theory and some experimental results (passive mode). It does not lead into the ignited mode and in this it appears to contradict Talaat's[7] contention regarding volume ionization.

<u>Discussion</u>

The models presented above have many features in common:

1. Sheaths (of zero thickness) at the electrodes

2. mean free path independent of energy

3. neutrality of plasma

4. Maxwellian velocity distribution

The results, however, even though in close agreement with their respective experiments, are quite different, and sometimes even contradictory, as in the case of volume ionization [6, 11, 12, 15]. This might indicate a need for an extremely critical and careful review of these models as well as the experimental data. In addition, it seems that the inclusion of sheath thickness, as well as variations of the mean free length with energy, might lead to more accurate and more general results.

B. Ignited Mode

Regarding the arc mode, one might preface with a quote[13] "As of today neither the atomic cross sections and constants nor the fundamental understanding of the basic process involved is sufficient to permit a satisfactory description". This author concludes that the operation in this mode is "definitely not understood", and suggests studies leading to the understanding of ionization mechanism, thermalization, and energy balance as fruitful area of research in exploring the arc mode of operation.

A reasonably successful model has been developed by Hernqvist[14]. He postulated a positive sheath at the collector, and a double sheath at the emitter, negative immediately adjacent to the emitter. The dominant ionization process is considered due to cumulative ionization, with ions formed by collisions of second kind. In addition, it is assumed that due to resonance trapping of the radiation, the effective lifetime of the excited states is three orders of magnitude greater than the natural lifetime. These assumptions lead to a model which shows good agreement between the theoretical and experimental I-V curves, normalized to the saturation current, for values of $(I/I_s) < .4$.

Witting and Gyftopoulos[15] use a model similar to that of Hernqvist[14]. Their results compare quite favorably with experimental data over a wide range of I-V values. The best results, however, appear to be those of Carabateas and Kniazzeh[11], who used a model quite similar to those described above.

Discussion

As in the case of passive mode models, the models used in the ignited mode have many features in common:

1. trapping of radiation

2. ionization via collisions of second kind

3. double sheath at the emitter, and positive sheath at the collector.

The results of analyses of these models do not vary as much as those in the passive mode; the variations, however, are such that again a critical review of the respective analyses is recommended. Further, the recommendations of Jarvis[13] seem a reasonable path for study, as well as consideration of photon diffusion.

Conclusions and Recommendations

Two basically different models describe reasonably accurately the two different modes of operation of plasma diodes. The most important features appear to be in inclusion of sheaths for both models, surface ionization for the passive mode, and volume ionization via collisions of second kind for the ignited mode. Except for the consideration of the effective life times of excited states, the model of Talaat [6] seems to offer the best description of the entire range of operation, whereas the other models apply either to one or the other. In spite of the similarity of the respective models, the results seem to fit only some selected experimental results. The I-V curves resulting from these models are quite different.

These considerations indicate that several study programs, independent of each other, might provide useful contributions in the area of thermionic energy conversion.

The first to suggest itself is a critical review of the different results from very similar models, and a unification of the results. Though this study may not necessarily lead to an original contribution, the results would be extremely useful to the workers in the field.

Another area of investigation would be devising a model which would successfully account the transition between the modes, as well as the characteristics in a given mode. Concentrating on the transition region itself may lead to a model which would describe the transition region accurately as well as the two modes as limiting cases. This represents a rather formidable task since in addition to ionization mechanism and photon diffusion, also patchy work functions, field effects at the electrodes, and the thickness variations of the sheaths may play a significant role. The effects of these phenomena could be investigated independently, so that their significance could be assessed independently.

The most immediate of these seem to be the sheath thickness and patchy work functions. The effects of the former are necessary in order that more accurate measurements on cross sections be made to enable a better understanding of ionization mechanism; and those of the latter, in order that the behavior of the emitter be better understood in presence of emitter sheath fields, as well as work function variations.

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Appendix F. Thermal Energy Storage - Materials

The differential thermal analysis apparatus has been completed and is in working condition. Calibration experiments are in progress on the pure salts MgF_2 and CaF_2. The differential thermal analysis apparatus consists of a platinum -40% Rhodium wound furnace, which can give temperatures up to 1750°C, a programmed controller with silicon controlled rectifier to raise the temperature of the furnace at a desired uniform rate, an adjustable zero, and adjustable range recorder for recording the temperature and a recorder with a ±5 mv range for recording the differential E.M.F. The differential E.M.F. is amplified by a D.C. amplifier before feeding to the recorder.

The desired uniform heating rate of the furnace is obtained by comparing a D. C. voltage to the thermocouple E.M.F. on a proportional controller which in turn regulates the power to the furnace. The D. C. voltage signal is varied by means of a motor driven cam. By this arrangement, it is possible to raise the temperature of the furnace at uniform rate from 3° to 20°C per minute. Lower heating and cooling rates have been achieved by lowering the rotation speed of the cam. The adjustable zero and adjustable range recorder can record the temperature accurately within ±1°C and is capable of internal standardization.

A reaction tube 1.5" in diameter and 42" long is fitted in the furnace tube. To one end of the reaction tube is attached a standard glass joint cone, the socket of which contains a positioned thermocouple sheath. A Pt-40% Rh wire loop, to hold the sample, is suspended from the thermocouple sheath. By having this type of arrangement it is possible to keep the position of the sample constant inside the furnace. The thermocouple sheath has six holes, of which two are used for a thermocouple for the programmed controller and three for the differential thermocouple. The samples are held in a coil of Pt-40% Rh wire suspended from the thermocouple sheath, the coil being grounded through the remaining hole in the sheath. Stray voltages have been a persistent problem but they have now been eliminated by fitting grounded conductive sheaths over all external leads and by winding a grounded platinum wire down the thermocouple sheath.

Work has been started on the binary and ternary systems outlined in the previous report.

Work is continuing on the construction of the diphenyl ether dropping calorimeter described in the previous report. The circuitry and head design of the calorimeter is being modified so that high temperature differential thermal analysis can be carried out within the furnace chamber. This is to be achieved by incorporating a saturable core reactor in the heating circuit and controlling this by the basic instrumentation of the previously described D.T.A. apparatus.

The galvanic cell apparatus for the determination of partial molar properties of the fluoride melts has been almost completed. Work is in progress on cell design and trial procedures based on the chlorides are being begun.

As the volume change on melting of energy storage fluids is likely to be of great importance in the design of systems, it is intended to construct suitable apparatus for such measurements. The design of the apparatus will be begun as soon as the calorimeter is in operation.

Appendix G. Thermal Energy Storage - Heat Transfer

The transient heat transfer problem associated with thermal energy storage is quite complicated, primarily because the material of interest becomes partially translucent at the temperatures under consideration and therefore the mode of heat transfer consists primarily of simultaneous conduction (phonon conduction) and radiation (photon conduction). The problem is further complicated by the fact that heat is transferred through the material where both liquid and solid phases are present. In addition to the problem of different phases, effects appear at the interfaces between the solid or liquid material and the container wall. It is quite clear from the above considerations that the mode of heat transfer in the system under consideration is neither a simple conduction nor a radiation but consists of both occurring through a material consisting of solid and liquid phases. Further, the transient state data is required. In the literature, even the data for the simple conductivity of these materials at the desired temperatures is not available, except that the thermal conductivities of BeO, CaO, MgO and Al_2O_3 in their solid states are reported at 1670°K as 0.0362, 0.0174, 0.0144 and 0.0131 cal $sec.^{-1}$ cm^{-1} $°C.^{-1}$ respectively.[1] Also, the thermal conductivity of "salt A" (11.5 mol -% NaF, 42.5 mol -%KF and 46.0 Mol. -%LiF) in the liquid phase for temperatures of 490°C to 850°C is given as 0.0057 to 0.0129 cal $sec.^{-1}$ cm^{-1} $°C^{-1}$.[2]

In view of this situation, it has been decided to design the initial experiments to measure the thermal conductivity of the selected thermal energy storage material in the solid phase, under the conditions of steady state heat transfer. In the process to be adopted, heat is passed from an external heater through the cylindrical specimen to a heat sink along its axis. Conductivities can be determined from the radial temperature drop across the specimen and the heat flow into the heat sink by the relation

$$k = \frac{q \ln {r_2}/{r_1}}{2 \pi L (\Delta T)} \qquad (1)$$

where r_1 and r_2 are the respective distances of the inner and outer sight holes from the axis and L is the length of the specimen over which the heat flow is measured.

Apparatus, slightly similar to Rasor's[3] and placed in a chamber with vacuum or controlled atmosphere, is as follows:

The heater Fig. 5 is a hollow graphite cylinder 8" long, 2.5" inside diameter, and 1/8" thick. The cylinder has a series of parallel grooves engraved on its outer surface, to a depth of half the wall thickness. The grooves are parallel to the base of the cylinder. There are two sets of grooves, each alternating from the other by 90° of arc. This arrangement prevents mechanical weakening of the heater. The heater is screwed into two carbon blocks of 5" diameter and 2.5" deep. The blocks have cylindrical holes equal to the diameter of the heater. The carbon blocks are connected through water-cooled copper tubes to a step down transformer with a secondary rating of fifteen volts at 600 amps. The primary of the transformer is connected through a variac to the power source. The heater is expected to give the desired temperature.

The heat sink, which also serves as a heater meter, consists of a 3/8 inch diameter stainless steel or molybdenum tube with walls 0.010 inch thick, along the axis of which is a 6 mm o.d. glass tube of 1 mm wall thickness. The sink tube extends along the axis of the heater from its bottom to the top up to the sight tube. Water or helium flows through the annulus between the inner and outer tubes. The external surface of the steel tube is blackened with carbon to increase radiant heat transfer and to eliminate adverse effects of non uniformity which may occur during operation of furnace. The inner glass tube is coated with coarse sand to obtain turbulence for better heat transfer.

Four sets of Platinel 1520/platinel 1786 (or other suitable materials depending on temperature) differential thermocouples are equally spaced around the inner tube in the annular space. The junctions of each are projected into the water stream and are separated by 1" in the region of the heat sink length opposite the center of the specimen.

The differential E.M.F. is therefore proportional to the temperature rise of the water as it passes through this region. Since negligible heat is expected to pass through the wall of the inner glass tube, the temperature rise of the water is proportional to the heat flow into that region of the heat sink. This heat meter is calibrated by passing an electric current through the outer tube and observing the thermocouple E.M.F. for a given electrical power dissipation in the corresponding length of the outer tube.

The cylindrical test specimen Fig. 6 is made of five circular disks stacked up one on top of the other. All the disks are 1/2" thick except the one in the center which is 1" thick. The disks are in the form of annular rings having an inside diameter of 1/2" and an outside diameter of 2". Tapered holes to the center plane of the center disk are made along the inside and outside periphery of the specimen as shown in Fig. 6. These holes are provided for measuring the temperatures with an optical pyrometer.

As may be seen from the figure in this method, heat is radiated from a graphite heater to the outer surface of the specimen. This heat is then conducted radially to the surface of the 1/2" diameter hole at the specimen axis, where it is radiated to a water cooled heat sink placed in the hole. The radial heat flow, q, through the central disk of 1" thickness is determined by measuring the flow rate and temperature rise of the cooling water in the corresponding section of the heat sink. The radial temperature drop ΔT is determined with an optical pyrometer by measuring the temperatures at two different radii through the sight holes penetrating to the central plane of the central disk.

From the quantity of heat passing through the sample and the radial temperature drop, the conductivity is determined by equation 1. The first set of experiments is designed for the conductivity measurements of the material in the solid state. Ultimately, the apparatus is to be modified to measure the conductivities in the liquid state too. After gaining knowledge of the conductivities of liquid and solid material, attempts will be made to determine some relation by which conductivities can be predicted for a material in solid and liquid phase at equilibrium.

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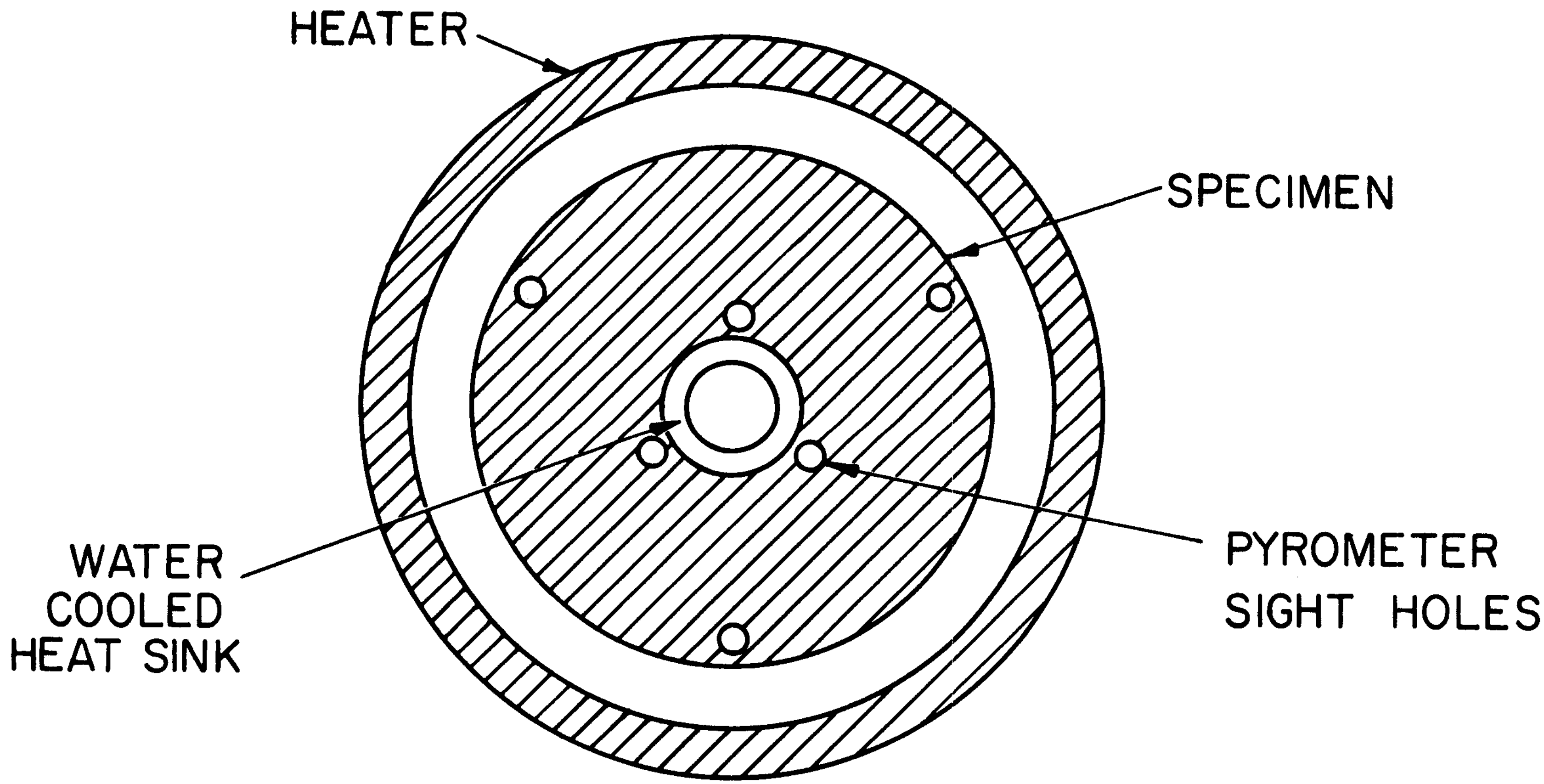

FIG.6 Configuration for thermal conductivity determination by external heating. Ref.2

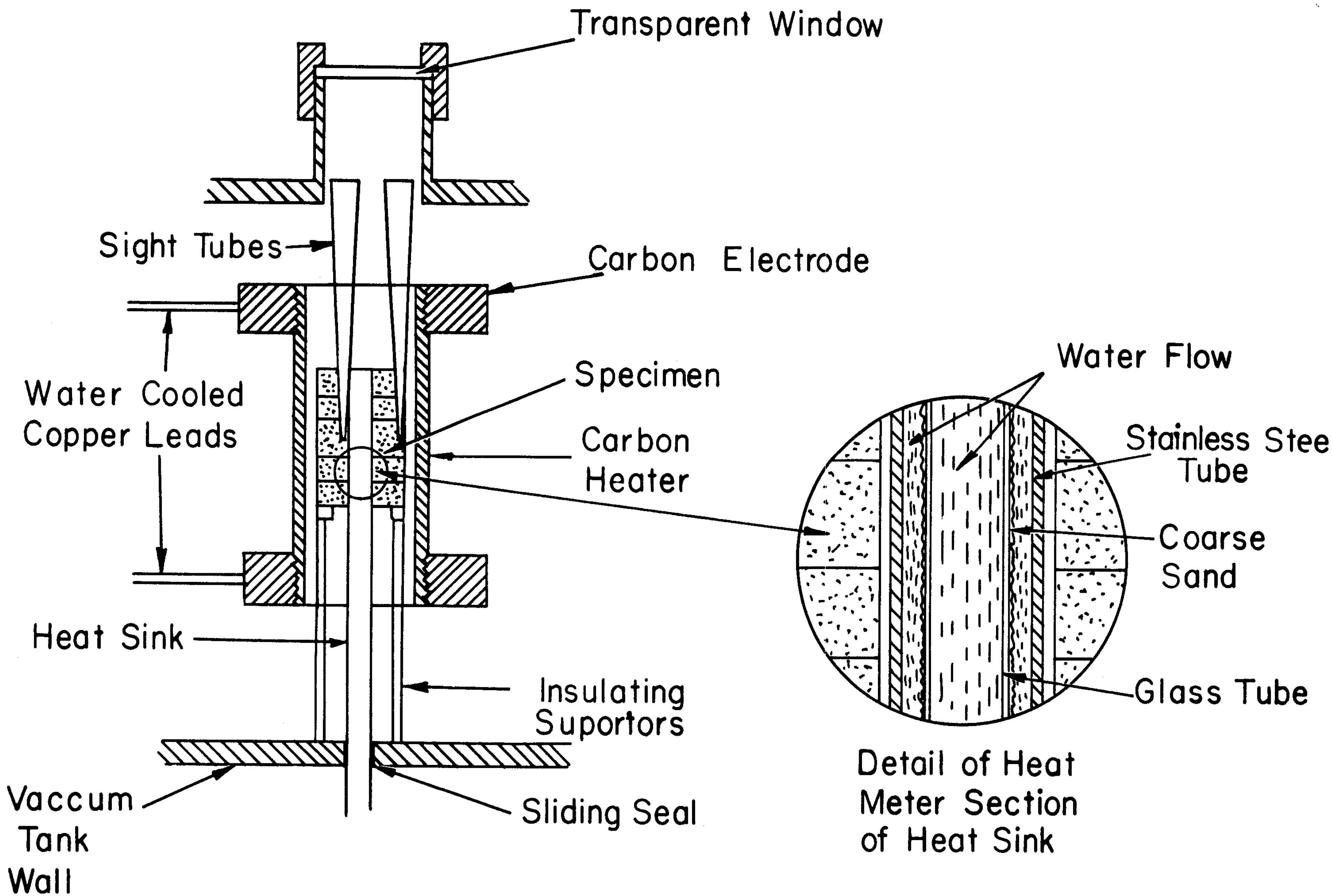

FIG.5 CONDUCTIVITY APPARATUS

Appendix H. Systems Considerations of Solar Powered Heat Engines with Thermal Energy Storage

Comments on the Development of Solar Powered Space Power Systems with Thermal Energy Storage

by

Manfred Altman

Introduction

This report is a summary of presentation made by the author before personnel of NASA-Lewis, TRW, and EPL. The purpose of this presentation was to outline the methodical, systematic approach to the analysis and development of solar powered space power systems which utilize thermal energy storage.

The primary aim of this presentation was to demonstrate how a consideration of the entire system including the solar concentrator, the heat receiver including thermal energy storage, the energy converter, and finally the radiator can lead to the isolation of problem areas whose solution must be found, and that a careful approach to these research problems is necessary to insure that the data which are obtained will be used in future system design and not be confined solely to the particular system under consideration at any one time.

What the Vehicle Designer or the Power Plant Designer Needs to Know

1. The vehicle designer who has to select a power plant needs the ability to make trade-off studies between different power systems.

2. In order to accomplish this, he must be able to optimize different systems for his specific application.

3. This makes it necessary to have a mathematical model of all the components of such a power system.

4. Ideally, a hybrid computer system would be used to provide a realistic analogue of the system.

5. It must be recognized that the eventual design point will be determined by the system transients and not steady-state conditions.

6. This implies that the analogue system must be able to simulate both start up as well as component failure conditions.

It is now pertinent to raise the question whether this type of analysis can be performed at this time with solar powered heat engines including thermal energy storage.

State of the Art

Solar Concentrators

The discussion on solar concentrators by Dr. George Schrenk, which is appended to this report, makes it clear that we do now possess the analytical ability to describe the performance of solar collectors adequately. Moreover, the results of the solar concentrator analysis include the distribution of heat sources on the inside of the heat receiver cavity.

Heat Receiver - Thermal Energy Storage

It must be recognized that the external geometry of the heat receiver will vary greatly depending on the specific system which is used. For instance, in the case of thermionic systems, the heat receiver might have cones projecting into the cavity. The reasons for this are that reliability considerations suggest that separate storage vessels should be used, and the fact that heat transfer considerations place a premium on large surface areas.

It is seen from the above that a conflict exists between the design of the cavity to minimize temperature drops through the thermal energy storage fluid on one hand and re-radiation losses on the other.

It is equally clear that it is not possible to separate the solar concentrator from the heat receiver in any optimization scheme, and an optimization procedure will have to include not only the solar collector and heat receiver but the converters as well. The impossibility of optimizing the various components separately is further illustrated by the fact that the re-radiation losses are going to be dependent not only on the external geometry of the heat receiver but also on the temperature of the inner surface of the heat receiver. The inside wall temperature of the heat receivers is going to depend on the physical, chemical, and transport properties of the thermal energy storage used, as well as on the particular orbit and conversion system which is used. Let us next consider what is known about possible thermal energy storage fluids.

Storage Fluids

Ideally, one would like to have available a variety of thermal energy storage fluids with melting points covering the temperature range of interest. Systems optimization then would include a particular thermal energy storage fluid as one of the perimeters to be varied. At the present time very little is known about suitable thermal energy storage fluids and the result of this has been that the thermal energy storage fluids is selected and the system is optimized for this particular compound. Because of this, it appears to this writer that one of the most important things which ought to be done in the immediate future would be to obtain the characteristics of a great many compounds and binary and ternary eutectics, which appear to be promising for most of these compounds. Phase diagrams have not been determined for many of these, so that the melting points are not known. The uncertainty in the melting point makes it very difficult to estimate the heat of fusion since predictions of heat of fusion are commonly made on the basis of entropy of fusion which requires a knowledge of the melting point of the eutectic mixture. Basically, the thermo-physical properties and transport properties of the thermal energy storage fluids which are needed are the melting point, heat of fusion, densities, volume changes, conductivities, thermal radiation effects, and container compatibility. It is unfortunately true that for the compounds of interest none of these properties are readily available.

A further difficulty exists in that properties of compounds at very high temperatures are very difficult to obtain. One example of this is the estimation of heats of fusion. One way of estimating heats of fusion is, as has been pointed out before, the use of the entropy of fusion. It is however possible to use a much more accurate method for the estimation of the heats of fusion. This method has been presented by a member of the Institute for Direct Energy Conversion at the 1963 National Heat Transfer Conference (Ref. 1). If one examines the results of the predictions of these two methods, one finds startling discrepancies in the results of the two. For example, the predicted heats of fusion for the binary eutectic of lithium fluoride and magnesium fluoride are 185 cals./gm. using the entropy of fusion method, whereas, the "exact" calculation results in a calculated value of 220 cals./gm. In view of the fact that experimentally measured quantities of heats of mixing and similar measurements were used in the so-called exact method and further, since the results of the two computations for this particular mixture would be expected to result in very good agreement, one can only conclude that one or several of the measured quantities are in error.

Another difficulty which must be watched out for is illustrated by the two compounds calcium fluoride and magnesium fluoride. Because of the similarity in structure of these two compounds one would expect that the heats of fusion ought to be very close to one another. It turns out, however, that the experimentally determined heats of fusion are 91 cals./gm. for calcium fluoride vs. 224 cals./gm. for magnesium fluoride. This would indicate that in all likelihood calcium fluoride exhibits a metastable state. Clearly, then, one has to be on guard as far as other compounds are concerned to make sure that such metastable states do not exist. One way to determine definitely whether such a state does indeed exist would be to determine the heat of fusion of a mixture of calcium fluoride and magnesium fluoride. In such a mixture it is not likely that calcium fluoride would exhibit such a metastable state, and therefore, one should expect to find a combined heat of fusion of the mixture to be closer to the high value corresponding to magnesium fluoride.

An examination of various available compounds tends to indicate that the binary eutectics of lithium oxide with beryllium oxide, magnesium oxide, and calcium oxide, ought to be very good from the point of view of high heats of fusion over a considerable temperature range. Yet, no data on these compounds are available.

To summarize, then, we must admit that sufficient data to allow a good systems optimization is not yet possible because of the lack of suitable data of possible thermal energy storage fluids. Apart from the thermo-physical properties of thermal energy storage fluids, it is also true that very little is known about their transport properties, particularly thermal conductivities and effective diffusivities. One of the important factors which must be considered is the amount of finning which would be required for adequate heat transfer. This depends partially on whether the fluid tends to wet the walls or not, since zero gravity effects must be considered. An additional important variable is represented by the contact resistance between the fluid and the heat transfer surfaces, which, for the types of fluids of interest, are not known at all. The volume changes on melting and solidification will obviously effect the amount of finning. An additional great uncertainity is the effect of the translucency of these materials. It may be possible to have a much greater effective thermal conductivity then would correspond to conduction alone. In view of the fact that radiation is expected to be extremely important, it becomes essential to determine the effect of long periods of operation on the translucency of materials. It is possible that even very small amounts of impurities might change the radiation properties of the materials considerably.

It should be clear in view of what has been said above that at this particular stage of the game the vehicle designer or the systems designer does not possess all the data which he should have to make meaningful systems optimization studies for purpose of selecting a specific power plant for a specific mission.

It is obvious, however, as to what research programs should be undertaken to provide the necessary data.

The first step ought to consist of a systematic investigation of the phase diagrams, thermo-physical and transport properties of likely compounds and their eutectic mixtures. In addition to these basic determinations, it is indicated that certain tests ought to be made to determine our ability to predict the performance of heat receiver solar collector combinations. It seems to this writer that a great deal could be learned by coupling a heat receiver with a cavity with very thin walls. The experimentally measured temperature distribution within the cavity should be very helpful in assessing the accuracy of our analytical methods. These tests may later on be augumented by the use of thick walled heat receivers which would tend to minimize the temperature variation within the cavity, and which would therefore, simulate the presence of thermal energy storage material. After completion of these tests, the final step would then be a test of heat receiver-solar collector unit which would include thermal energy storage and which would be capable of testing these combinations under actual transient conditions.

A final comment might be made to the effect that an opportunity exists to use the programs in existence like Sunflower and the Solar Powered Brayton Cycle Study to provide data which would be useful not only for the present application but for future applications. It is believed that attention to general applicability at this stage of the game would end up in a considerable saving of time, effort, and money when later applications are being considered.

Program for Work at the Institute for Direct Energy Conversion

I. General

It appears that our biggest contribution can be made in the following areas:

1. In providing NASA with precision measurements of the various thermo-physical and transport properties which are needed.

2. To develop "ingenious" methods of making these measurements at high temperature. A typical problem area might be the development of reliable thermal conductivity measurements which include radiation affects by the use of monochromatic photons.

3. To provide complete measurements such as complete phase diagrams which may be of general use at some future time.

II. Specifics

A. Theoretical Work

1. The development of mathematical methods for the analysis of thermal transients in heat receivers.

2. The prediction of thermal radiation effects on the effective conductivity of materials.

3. Better prediction of heats of fusion than is provided by the use of entropy of fusion.

B. Experimental

1. In the materials area an effort will be made to produce the phase diagrams for the following binary mixtures:

   a. Lithium oxide-magnesium oxide

b. Lithium oxide-calcium oxide

c. Lithium oxide-beryllium oxide

d. Beryllium oxide-magnesium oxide

e. Beryllium fluoride-beryllium oxide

f. Magnesium fluoride-magnesium oxide

It is also intended to study the ternary eutectics of lithium oxide with other high-melting mixtures.

2. Determinations of Heat of Fusion

3. Volume Changes on Solidification

4. Determination of Transport properties of the above materials including effective conductivities, as well as photon absorption studies.

Experimental Equipment

Three major pieces of equipment are being assembled for the experimental phase of this program. They consist of an isothermal calorimeter for the precision measurements of heat of fusion, a differential thermal analyzer for the determination of phase diagrams, as well as the rough determination of heats of fusion, and, thirdly, a thermal conductivity apparatus which will be suitable for the determination of transient properties as well. The details of the differential thermal analyzer and the isothermal calorimeter are presented below because they represent the type of measurements which we will be capable of performing at the Institute. It should be noted that it is our intention to make this equipment available to NASA and its contractors at any time should it be necessary to provide quick measurements of compounds of immediate interest.

The details of the differential thermal analyzer are shown in Figure 1 and 2. The equipment has been assembled and testing is being initiated. It consists primarily of a reaction tube whose temperature is controlled by a programmed controllor in such a way that its temperature increases as a linear function of time until a phase transformation takes place. Recorders have been arranged in such a manner that both total and differential EMF's can be recorded. Details of the reaction tube and furnace are shown in Figure 2.

The isothermal calorimeter is depicted in Figure 3 on which the details of construction are shown. Its principle of operation is that the sample is melted in the upper part of the furnace and is dropped into the calorimeter itself in such a way that heat losses to its surroundings will be completely negligible. The calorimeter itself consists of a tube which is surrounded by diphenyl ether. The entire vessel will be taken up by this diphenyl ether by the introduction of mercury in the bottom of the vessel. At the initiation of a measurement the diphenyl ether in contact with the inner tube will be frozen by the addition of some dry ice to this tube. After the sample drops into the bottom of the tube, it will lose heat to its surroundings and melt the diphenyl ether surrounding the tube. From the expansion of the diphenyl ether as it is melted, it is possible to calculate the total amount of heat liberated. The increase in volume due to melting will be measured by the displacement of the mercury column. This apparatus is in the final stages of assembly and it is expected to become operational by February 15, 1964.

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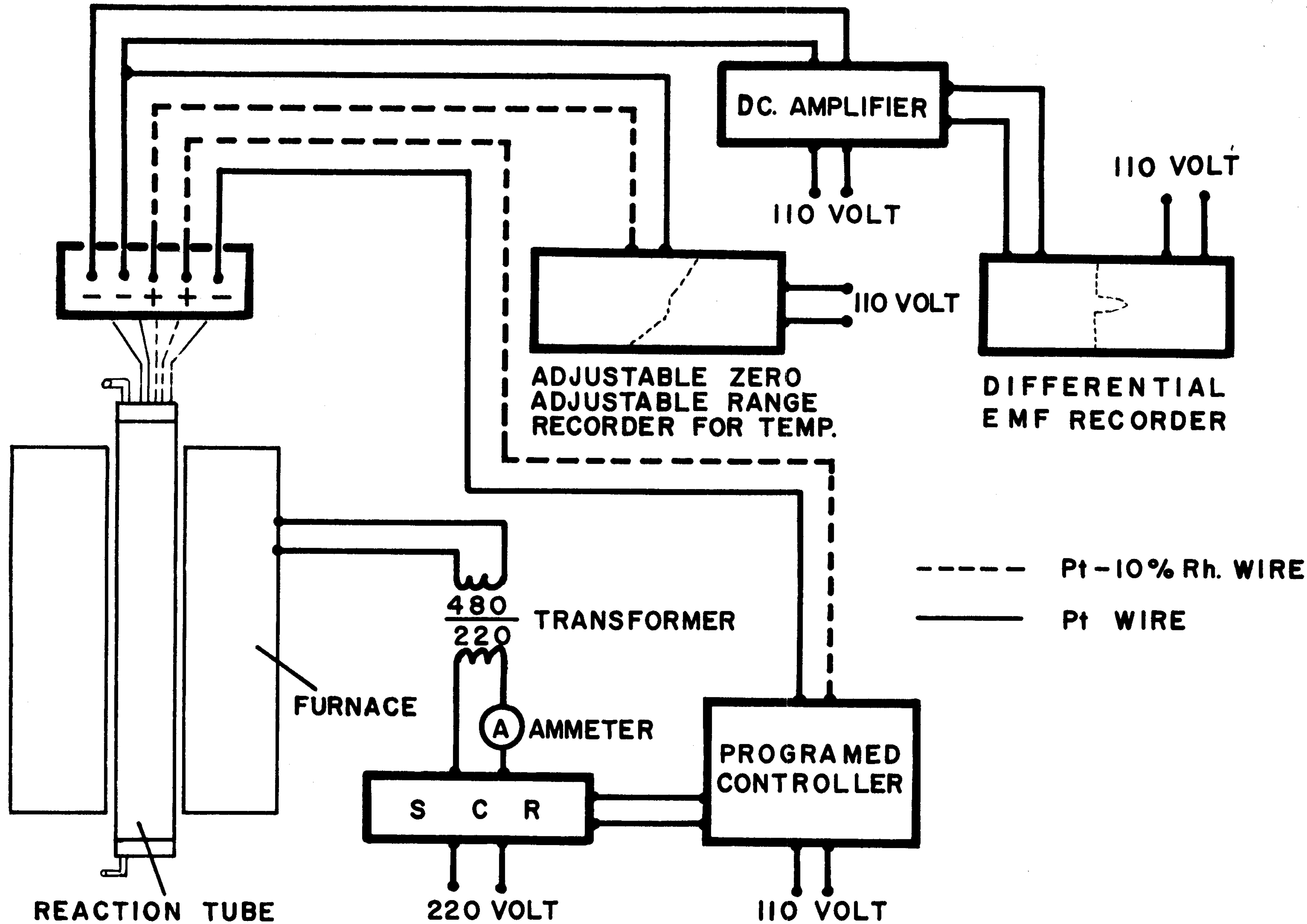


FIG. 1 SCHEMATIC DIAGRAM FOR D.T.A. APPARATUS

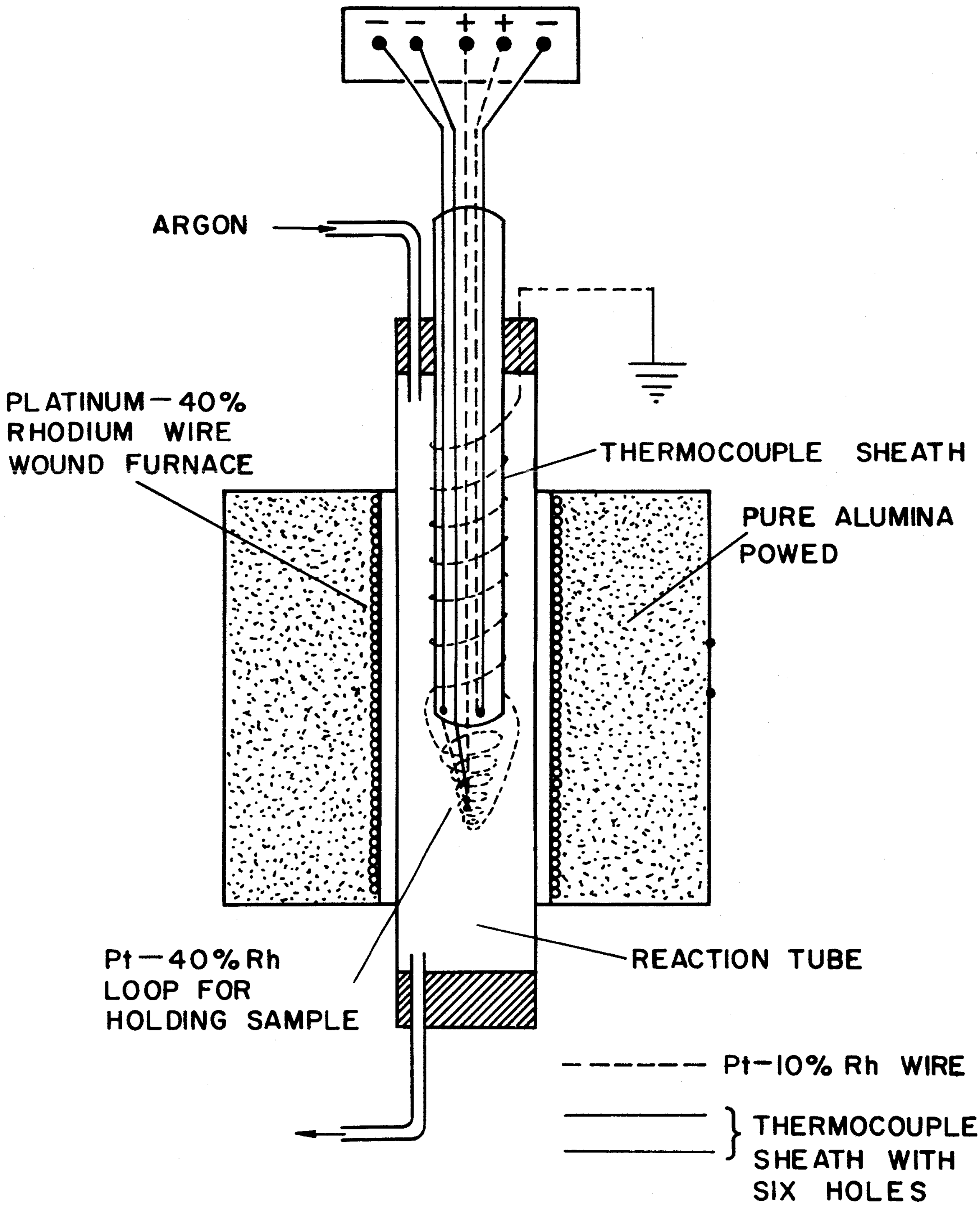
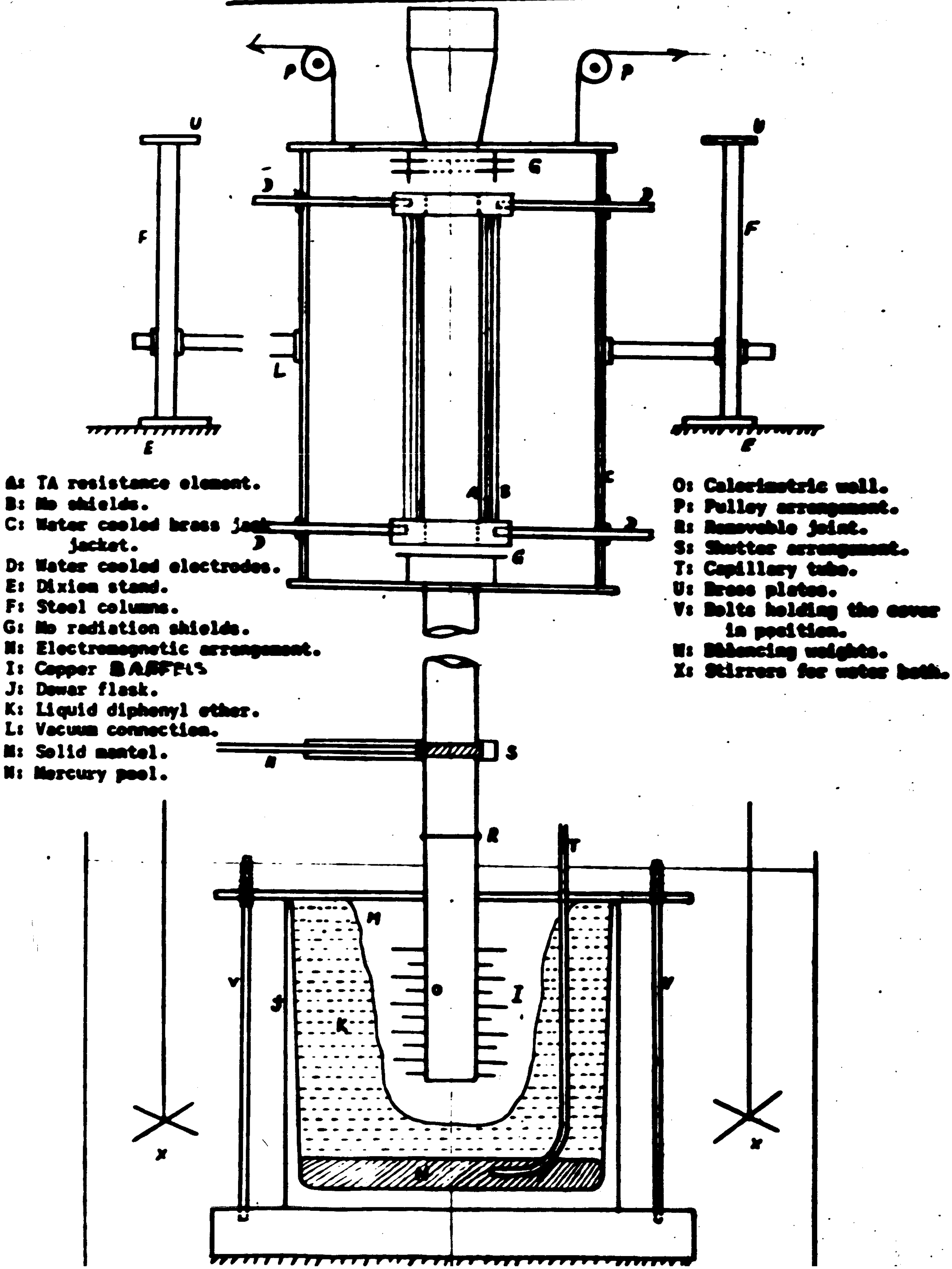


FIG. 2 DETAILS OF THE D.T.A FURNACE

ISOTHERMAL CALORIMETER



Comments on Analytical Capabilities for Predicting the Performance of Solar Collectors and Heat Receivers

by

George L. Schrenk

Fundamental to the analysis of solar reflectors is the fact that the source (sun) is not a point source. Because of this fact the classical techniques of ray tracing no longer apply. Instead, cone tracing techniques must be used--as a cone can be used to represent the light coming from a small but finite source. The concept of cone tracing was introduced by F. Cabannes and A. Le Phat Vinh (1) in 1954 and by N. Hukuo and H. Mii (2) in 1957. Cabannes and Le Phat Vinh considered only perfect paraboloids. Hukuo and Mii also considered perfect paraboloids, but they then attempted to apply their results to real reflectors by introduction of a "scattering circle" concept--i.e., the reflected rays are statistically scattered in the focal plane uniformly over a circular region.

Hukuo and Mii were perhaps the first to apply statistics to predict real reflector performance by introducing a "scattering circle" concept. This concept was extended to the use of a normal distribution in the focal plane (in place of the uniform distribution of the "scattering circle" concept) by various groups late in 1960 (3, 4) and several papers have since been published on this by other authors (5, 6). It is important to point out that this concept applies a probability distribution to a scattering of points in the focal plane; thus, it is not possible to relate theoretically the probability distribution in the focal plane with the manufacturing procedures on the reflector surface. The alternative is to apply the probability distribution to the surface normals on the reflector. Physically, this is the most desirable approach; however, it is also the most difficult to implement. Perhaps the first person to try this type of approach was Silvern (7). His work, however, was plagued with several errors and numerous approximations. He assumed that finite rotations commute and he applied the normal distribution function incorrectly to angles. He did, however, obtain numerical results from his work. Since this time, in addition to the work discussed here, there have been several other attacks on this problem.

Fuller (8) formulated a mathematical approach to this problem. His work, however, presents several major problems: (1) he applied the normal distribution function incorrectly to angles, and (2) his work was never successfully programmed on a computer. General Electric (9) has also carried out analytical work to predict the performance of a reflector possessing a fixed specific surface error over the entire surface. No provisions were made to treat orientation errors and no introduction of statistics was made. General Electric, however, did achieve operative computer programs.

Theoretical work on optical analysis problems was started by this writer (under contract to Allison Div. G. M. C.) early in 1959. Initially cone tracing techniques were used to analyze conical serration Fresnel reflectors. This work, however, was restricted to perfect surfaces. Upon completion of this work (10, 11) in late 1960, work was started toward the analysis of actual solar reflectors.

From the start, the required model of a solar collector had to be as general as possible and had to be capable of analyzing both perfect and imperfect (actual) reflectors. Because of the necessary complexity of such a general model, from the very first the goals of this work were twofold:

1. Development of a mathematical model

2. Development of an operative computer program from this mathematical model.

The complexity of the many problems encountered can be appreciated by looking at the interim report (12), written in June 1961. Over a period of time, we were successful in developing the desired mathematical model for actual solar collectors (13, 14, 15). This model included provisions for treating random surface errors on the reflector surface and orientation errors of any size. Furthermore, almost all the approximations introduced by others into cone optics were removed. The approach to the development of the mathematical model was judiciously selected to result in a practical and useful tool for the design and evaluation of solar-thermal energy conversion systems. The operative computer program (D70E) for evaluating solar reflectors that was developed from these equations is practical and feasible from a computational (and computer running time) viewpoint.

Although the mathematical model applied to any conceivable reflector, the computer program (D70E) was designed to treat only paraboloidal reflectors, conical Fresnel serrations, spherical Fresnel serrations and/or any part of these reflectors. This initial work, however, was restricted to the determination of the magnitude of the energy distribution on any plane surface perpendicular to the optical axis.

In early 1963, a copy of this D70E program was purchased by Aerospace under contract No. 62-167. As already pointed out, the only restriction in this work to date was that it applied only to plane focal surfaces. Although the use of plane focal surfaces is convenient for a general study of solar reflectors, the results obtained are not in a convenient form for use in connection with a solar thermal energy absorber such as a cavity. In fact, the use of such results require that critical assumptions be made concerning the direction distribution of the energy density in the focal plane. Because of this, it was highly desirable to extend the previous analytical work to be able to calculate the energy flux distribution on any arbitrarily shaped focal surface (e.g., a cavity wall). With this extended capability, the mathematical model would then not only check the directional assumptions used but would also obviate the necessity for making any directional assumptions. The perfection of this generalized mathematical model would provide the solar power system designer with a mathematical tool that was heretofore unavailable.

This extended mathematical model was developed and perfected under contract AFO4(695)-335. As a result of this extended work all the approximations introduced into cone optics have been removed; it is now possible to calculate the energy flux distribution on any arbitrarily shaped focal surface from any arbitrarily shaped reflector surface. This model includes provisions for treating random surface errors on the reflector surface, orientation errors of any size, and vignetting* of reflected radiation by a cavity opening. No approximations were introduced; the model is accurate within the limitations of the numerical techniques of integration on high speed digital computers. An operative program (174B) for evaluating solar reflectors was developed; this program is practical and feasible from a computational (and computer-running time) viewpoint. This theoretical work and the accompanying computer codes are described in detail in reference 15.

*The term vignetting refers specifically to blockage of reflected light by a cavity opening. This in contrast to the term blockage, which is used to refer specifically to bloackage of incident light on the reflector. In addition to vignetting, provisions also exist for treating blockage of incident light.

Now a mathematical solar simulator--i.e., a detailed mathematical model of a solar collector--is a necessary and indispensable tool in any realistic systems study involving solar reflectors. More specifically, it must serve as the starting point for any analytical study of a solar power system involving solar reflectors. Because of the broad scope and generality of this model, its perfection now provides the solar power system designer with tools that have been heretofore unavailable.

The existence of this mathematical solar simulator is the first step necessary in any detailed study of a solar power system. The analytical capabilities discussed here are presently available; however, they are not as yet extensively being used. Instead, crude and often erroneous techniques are usually being applied. In the best interest of solar power systems it is imperative that the present existing capabilities be fully utilized.

Proper use of existing analytical capabilities can greatly expedite the development of solar power systems. This model can statistically predict reflector performance before a reflector is built, and, by using ray tracing data, it can predict the performance of a given reflector after it has been built. There are also many problem areas that can be accurately and thoroughly studied only by using this model--such as thermal stress problems (These problems must be studied for a specific design to arrive at an equation for the deformed surface of the reflector. Once the deformed surface is known, the present model allows prediction of the resulting energy flux distribution on any arbitrarily shaped focal surface.), etc. Thus, this theoretical work is of such generality that it can handle almost any problem concerning reflectors. The value of this analytical capability to the development of solar power systems can not be estimated; therefore, it is imperative that it be fully utilized.

Recently we have used this model to explore various problem areas concerning solar power systems--specifically systems consisting of solar reflectors and heat receivers (i.e., cavities). This work is limited to be exploratory in nature and will <u>not</u> constitute a detailed systems study on any proposed systems. It is being carried out in order to define clearly the various problem areas and to produce curves that will be representative of the results that one can expect to obtain from actual solar reflector and heat receiver systems.

Lambert's Law

The first problem area under exploration with this model is the interface between the solar collector and the cavity--namely, the cavity opening. The classical directional assumption made for this interface is that this opening can be treated as if it were a plane surface that emitted radiation according to Lambert's law (i.e., the cosine law). Until recently one could calculate the predicted energy flux only on plane surfaces, such as the cavity opening. The radiation passing through this opening was then assumed to obey Lambert's law for any detailed study of the cavity. Clearly this type of approach served to isolate the study and design of the cavity from that of the reflector.

With the recent perfection of the mathematical model described in reference 15, it is now possible for the first time to investigate this assumption. This question can be investigated in two ways. First, the actual directional distribution can be calculated. This is best done by looking at a hemispherical cavity located on the principal axis of the reflector with a small opening. Second, the actual energy flux incident on the walls of typical cavities can be calculated and compared with similar results obtained through the use of Lambert's law. This tells how important any deviations from Lambert's law will be for any proposed cavity configuration.

Let

σ_x = circumferential mean deviation of the reflector surface normals

σ_y = radial mean deviation of the reflector surface normals

I = concentration ratio of reflected light. Multiplication of I by the solar constant and the coefficient of reflection results in the actual energy flux/unit area incident on the focal surface point.

Figure 1 shows a sketch of the hemispherical cavity used to determine the directional distribution and the cylindrical cavity used to examine the importance of deviations from Lambert's law for a typical cavity.

For a perfect reflector ($\sigma_x = \sigma_y = 0$) Figure 2 shows a plot of I vs. cos θ for the hemispherical cavity of Figure 1. Figure 3 is a polar plot of these results that clearly shows the directional distribution. Figure 4 shows a plot of I along the walls of the cylindrical cavity. The opening of this cavity was arbitrarily chosen to collect 90% of the reflected energy. Lambert's law has also been plotted in these figures for the purpose of comparison. These results clearly indicate that Lambert' s law is invalid for perfect paraboloidal reflectors.

The same results have been obtained for a typical imperfect reflector where $\sigma_x = 5'$, $\sigma_y = 10'$. Figure 5 shows a plot of I vs. cos θ for the same hemispherical cavity; Figure 6 is a polar plot of these results to show the directional distribution; and Figure 7 shows a plot of I for the walls of the cylindrical cavity. Here, also, the opening was arbitrarily chosen to collect 90% of the reflected energy. These results clearly indicate that even for imperfect paraboloidal reflectors Lambert's law is invalid.

The lack of validity of the Lambertian assumption means that the reflector cannot be isolated and independently optimized from the heat receiver; instead, it must be studied as just one component of a proposed solar power system with the system being optimized from a systems view-point. Furthermore, the cylindrical cavity results shown in Figures 4 and 7 also indicate that the design of a solar power system on the basis of Lambert's law could lead to significant problems and/or failures. The shift in position and magnitude of the peak of I along the wall of the cylindrical cavity simply cannot be ignored. It must also be pointed out here that these results do not presently take into account blockage of the incident light by the physical structure of the heat receiver; they assume a full paraboloidal reflector with no blockage. The inclusion of such blockage is expected to lead to further deviations from Lambert's law.

Heat Receivers

Another problem area under exploration is the calculation of the performance of typical heat receivers. A computer program to calculate the performance of cylindrical heat receivers has been developed. The approach used in this work can best be described as an "open cavity" Fredholm integral equation approach. No specific directional distribution has been assumed in this approach; instead, it uses the actual energy flux on the wall of the cavity.

To understand this approach, consider the sketch shown in Fig. 8. Define

x	=	a coordinate specifying a point on the cylindrical cavity
$f(x)$	=	incident energy flux on the wall of the cavity
$T(x)$	=	assumed temperature distribution of the wall of the cavity
σ	=	Stefan-Boltzmann constant
ϵ	=	emissivity of the cavity wall
α	=	absorptivity of the cavity wall
$K(x,x')$	=	Kernel of the integral equation. This is a geometrical factor that describes the cavity geometry. It is an infinitesimal area view factor.
$\nu(x)$	=	total energy flux reflected and emitted from the point x of the cavity.

Assuming that the walls of the cavity are diffuse*, one obtains

$$\nu(x) = \epsilon \sigma T^4(x) + (1 - \alpha) \left[f(x) + \int_{\substack{\text{walls}\\ \text{of cavity}}} K(x, x') \, \nu(x') \, dx' \right]$$

Here the integral extends over only the material walls of the cavity--hence, the designation "open cavity" approach. Thecalculation of the kernel $K(x, x')$ for the cylindrical geometry is straightforward and will not be discussed here. The numercial solution of the Fredholm integral equation is carried out by using the well known Liouville-Neumann Series. A temperature distribution $T(x)$ is assumed and this equation is then solved for $\nu(x)$. When $\nu(x)$ is known, the entire performance of the cavity can then be calculated.

Some initial results have been obtained for a perfect 60° paraboloidal reflector (10' diameter) with a cylindrical cavity with a length of 4" and a diameter of 1.6" ($l/d = 2.5$). The diameter of the cavity opening was chosen to be 0.8" in order to collect 95% of the reflected energy.

Define

A	=	area of opening
Q_R	=	total energy reradiated out of the cavity opening
η	=	efficiency of the cavity = total energy entering the cavity / total energy conducted through the walls of the cavity.

*It is important to emphasize that the material walls of the cavity are assumed to emit and reflect radiation diffusely. Specular reflection has been neglected because the precise techniques of analysis have never been worked out here. Crude techniques of analysis do exist; however, accurate techniques that take into account the finite size of the solar source do not presently exist.

Figure 9 shows the results obtained for this cavity when it is assumed to be isothermal at $1000^{\circ}K$. Figure 10 shows the same results when this cavity is assumed to be isothermal at $1500^{\circ}K$. In both cases, Lambert's law was assumed for the directional distribution as these results were obtained before the correct distributions were available. These results are presently being obtained with the correct directional distributions.

The results shown in Figures 9 and 10 differ significantly from the usual engineering approach used in the design of solar power systems--namely that the cavity can be treated as a gray body ($\epsilon < 1$)*. Those who use this gray body approach argue that if the cavity opening were small, the cavity would behave like a black body. Hence, as the opening is made larger, the cavity ought to behave like a gray body. They have, however, neglected the important fact that this cavity is fundamentally different as it is driven by energy entering through the opening instead of through the walls. The results presented here offer perhaps the first realistic estimates of cavity performance (when the cavity is coupled to a solar reflector). They clearly show the importance of the absorptivity of the material surface of the cavity walls and point out that a gray cavity assumption is erroneous.

Results and experience that we have obtained clearly show that a very detailed cavity analysis must be made in order to accurately estimate cavity performance. Furthermore, since the incident flux distribution on the cavity wall is a function of the actual reflector used and since the cavity wall temperature distribution is a function of whatever connects to the cavity walls (thermal energy storage material, heat exchanger, etc.), the cavity <u>cannot</u> be studied and optimized independently. Instead, a systems approach must be utilized.

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*Specifically, it is usually assumed that the cavity losses can be separated into losses due to multiple reflections (these are often neglected) and losses due to reradiation effects from a gray cavity. Losses from multiple reflections, if included, are treated as corrections to gray cavity results. Now, from the basic integral equation it is clear that this decomposition into reflected and reradiated losses has no meaning--only the total has a physical meaning. Hence, it is meaningless to treat multiple diffuse reflection losses as a correction to the gray cavity reradiation losses.

It is important to point out here the work of Al Lowi and associates at Aerospace. They are performing the most extensive and realistic solar power systems study to date. Their system presently consists of a solar reflector, cylindrical cavity, and a gaseous heat exchanger. They are using the optical analysis techniques previously discussed to calculate the energy flux on the walls of the cavity. Their cavity analysis technique is basically the same as that described here, except they use a finite difference approach to the problem. Thus they use finite area view factors and invert a matrix to solve their cavity. They, however, take into account spectral properties by using spectral decompositions of the radiation. For the heat exchanger analysis, a thermal analyzer network solution is used. They perform an iteration between the cavity and heat exchanger routines to solve for the cavity wall temperature distribution. Their results (restricted to isothermal walls) agree with those we obtained by solving the Fredholm integral equation.

Their experience and results clearly show the importance and need for performing extensive detailed systems studies of solar power systems. Their efforts to date have only begun to "scratch the surface" -- thermal energy storage materials must be included, various cavity geometries must be studied, other types of heat exchangers and direct conversion devices must be used, etc.

The design of cavities for use with solar reflectors is still a very difficult problem area. Much remains to be done here. For example, the inclusion of thermal energy storage material has not yet ever been accomplished with any degree of analytical competence.) Many analytical problems must be met and solved before the analytical understanding and state of art here can even approach that currently possessed for solar reflectors.

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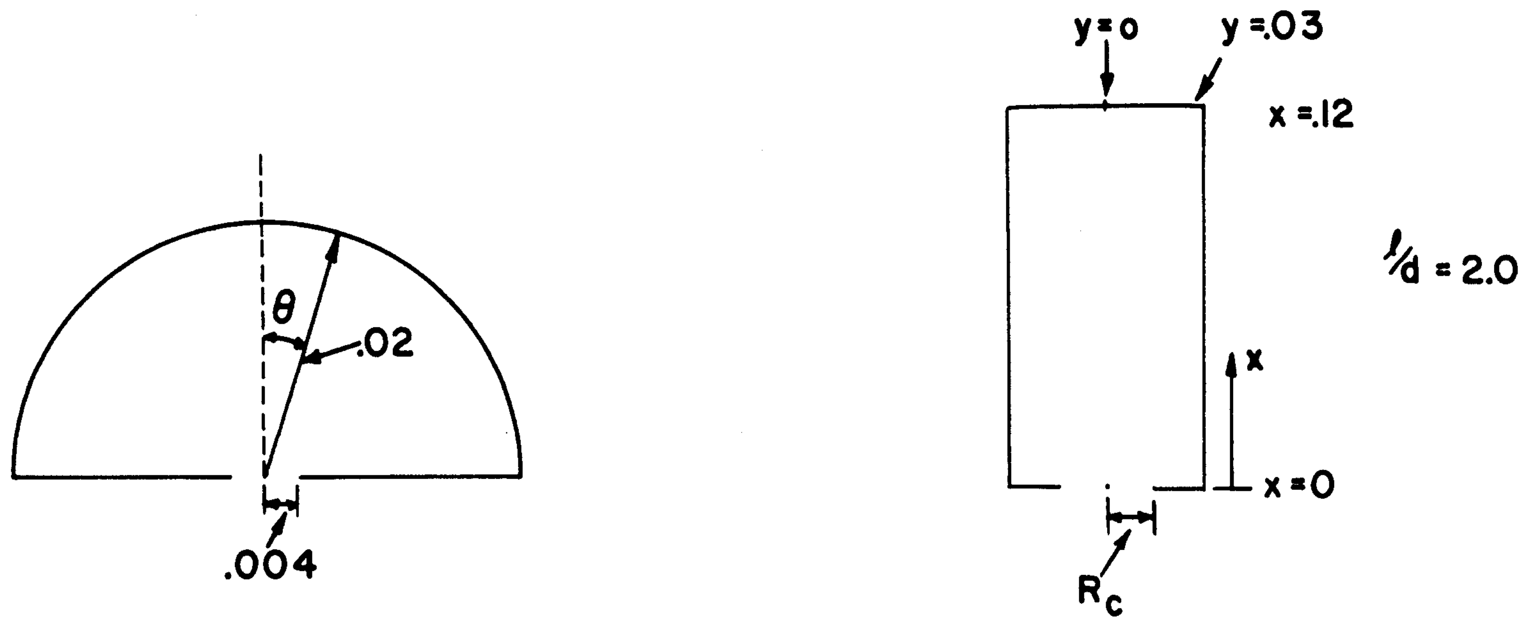

FIG. 1 The hemispherical and cylindrical cavities used to obtain the results in Figs. 2-7. The reflector used with these cavities was a 60° paraboloidal reflector with radius = 1.0.

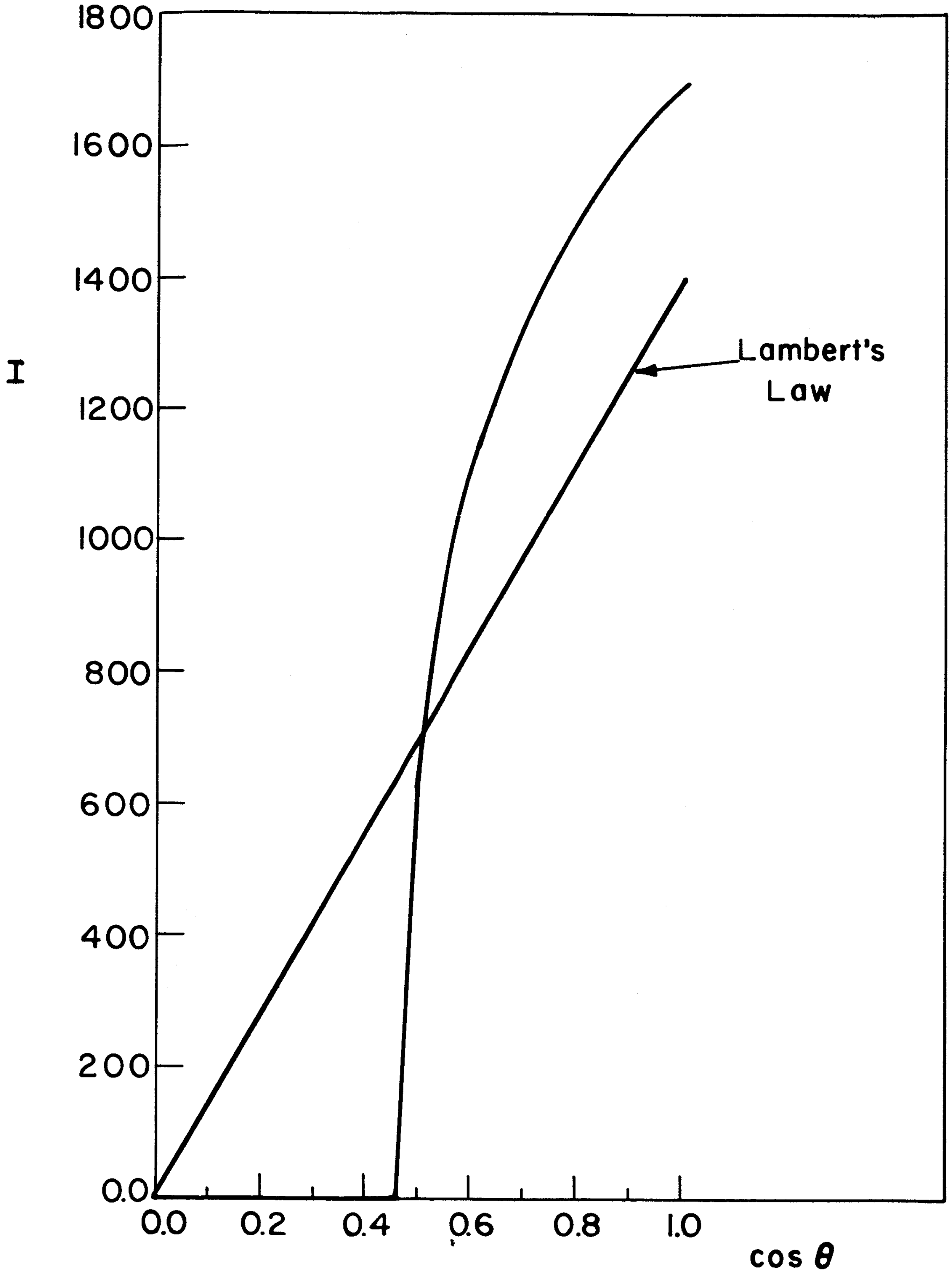

FIG. 2 Plot of I vs. Cos. θ for the hemispherical cavity of Fig. 1 for a perfect 60° paraboloidal reflector.

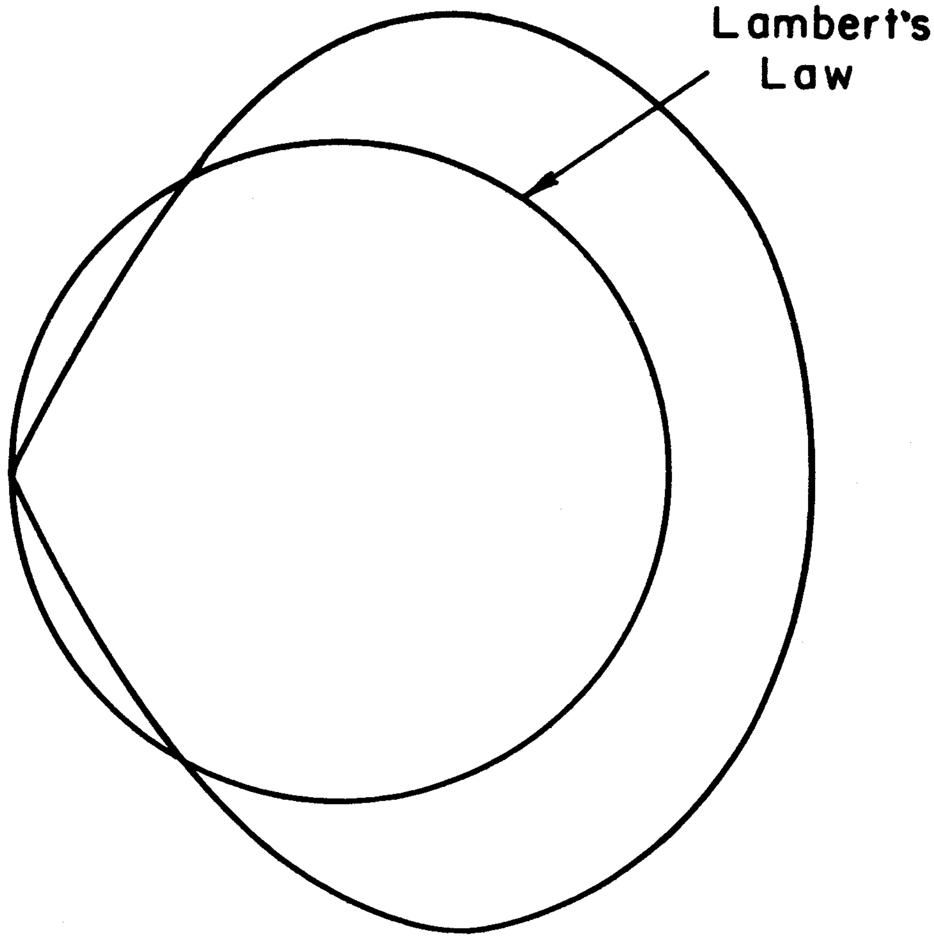

FIG. 3 Directional distribution for perfect 60° paraboloidal reflector.

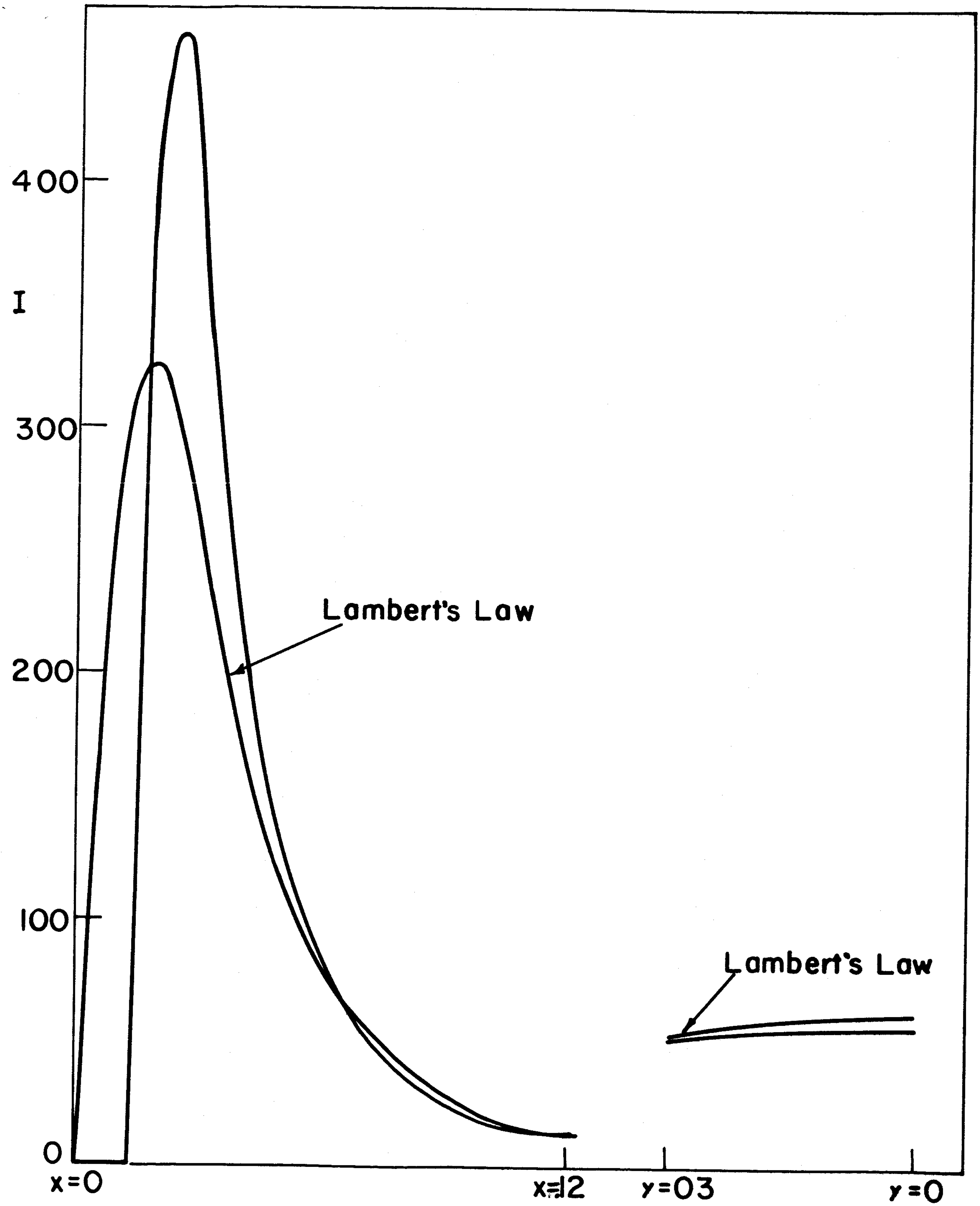

FIG. 4 Plot of I on the walls of the cylindrical cavity of Fig. 1 for a perfect 60° paraboloidal reflector. $R_c = .006$.

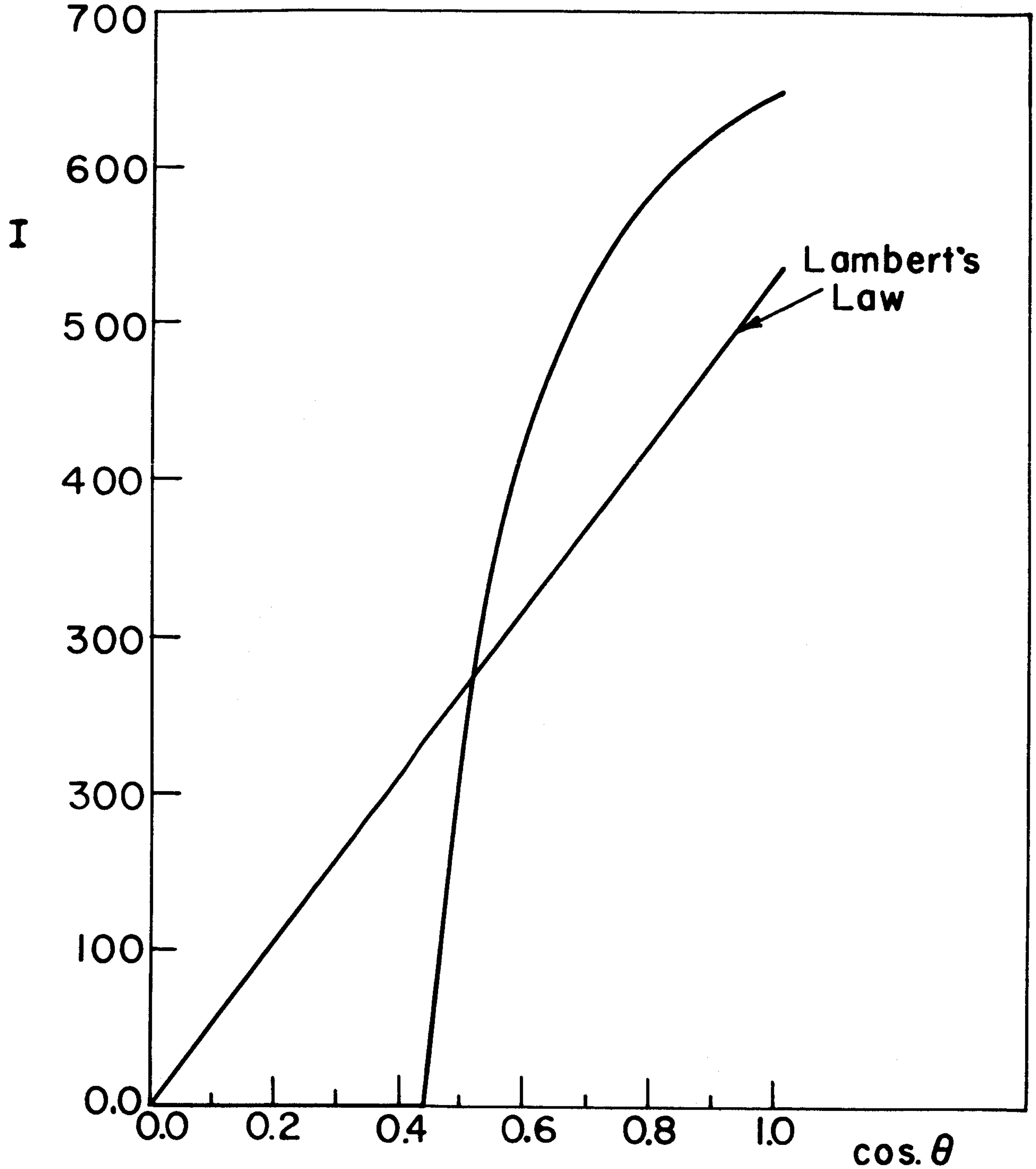

FIG. 5 Plot of I vs. Cos. θ for the hemispherical cavity of Fig. 1 for a 60° paraboloidal reflector with $\sigma_x = 5'$, $\sigma_y = 10'$.

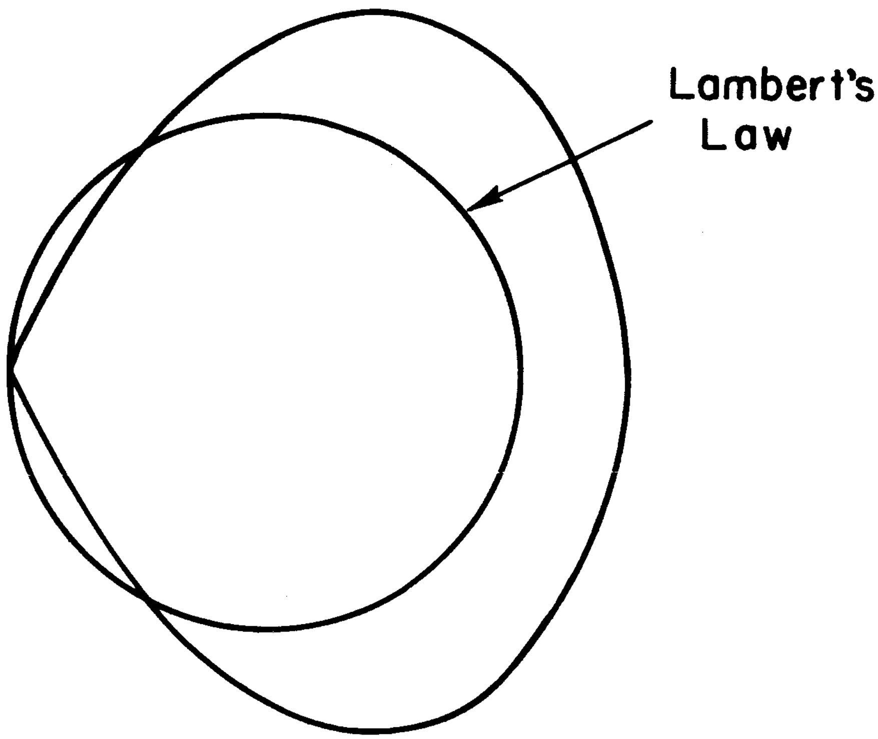

FIG. 6 Directional Distribution for a 60° paraboloidal reflector with $\sigma_x = 5'$, $\sigma_y = 10'$.

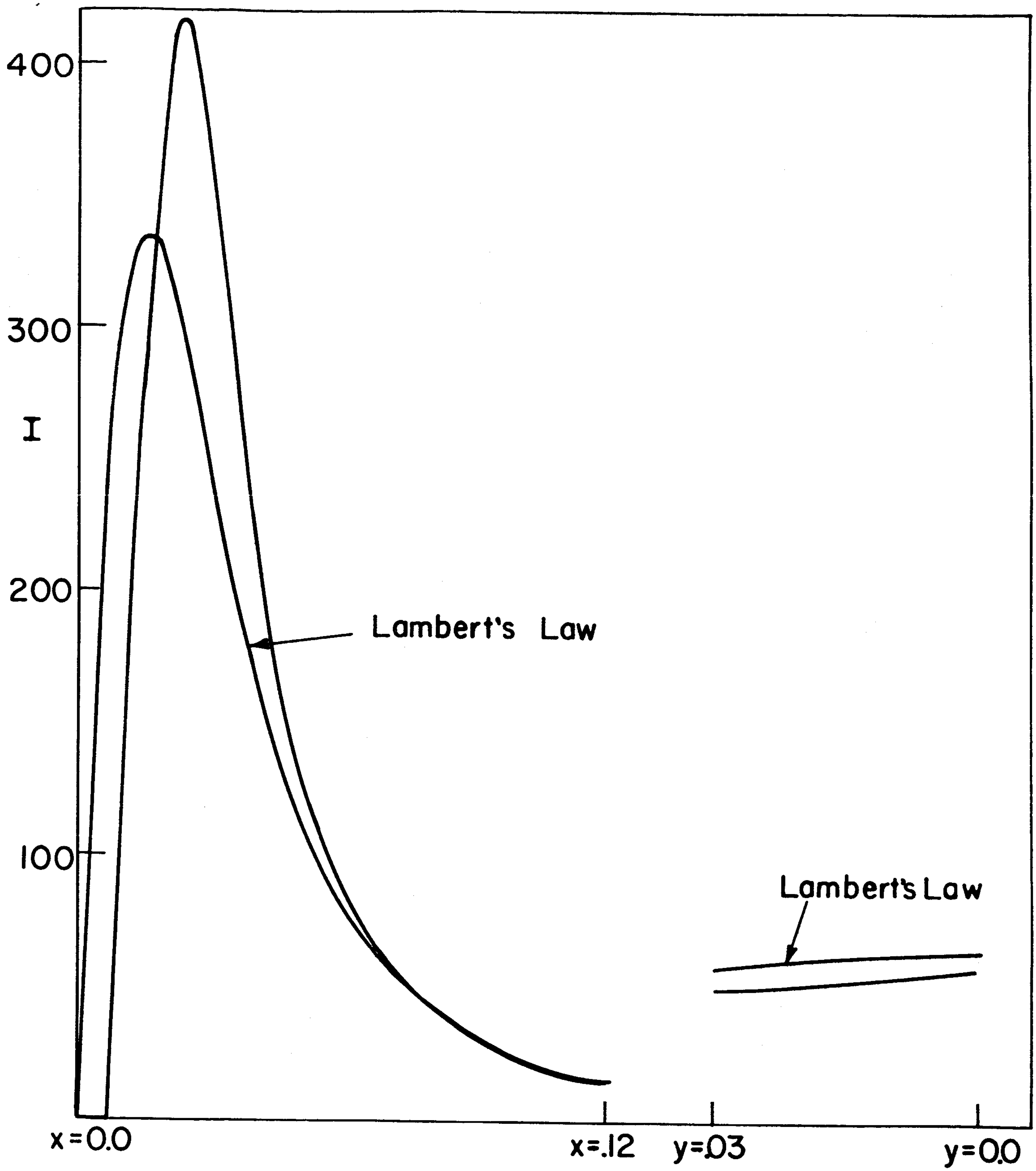

FIG. 7 Plot of I on the walls of the cylindrical cavity of Fig. 1 for a 60° paraboloidal reflector with $\sigma_x = 5'$, $\sigma_y = 10'$. $R_c = .017$

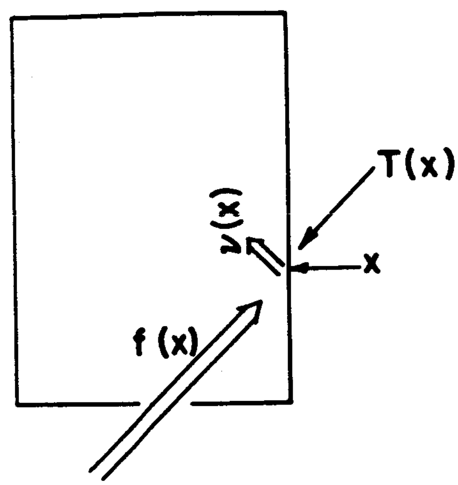

FIG. 8 Definition of terms for calculation of cavity performance.

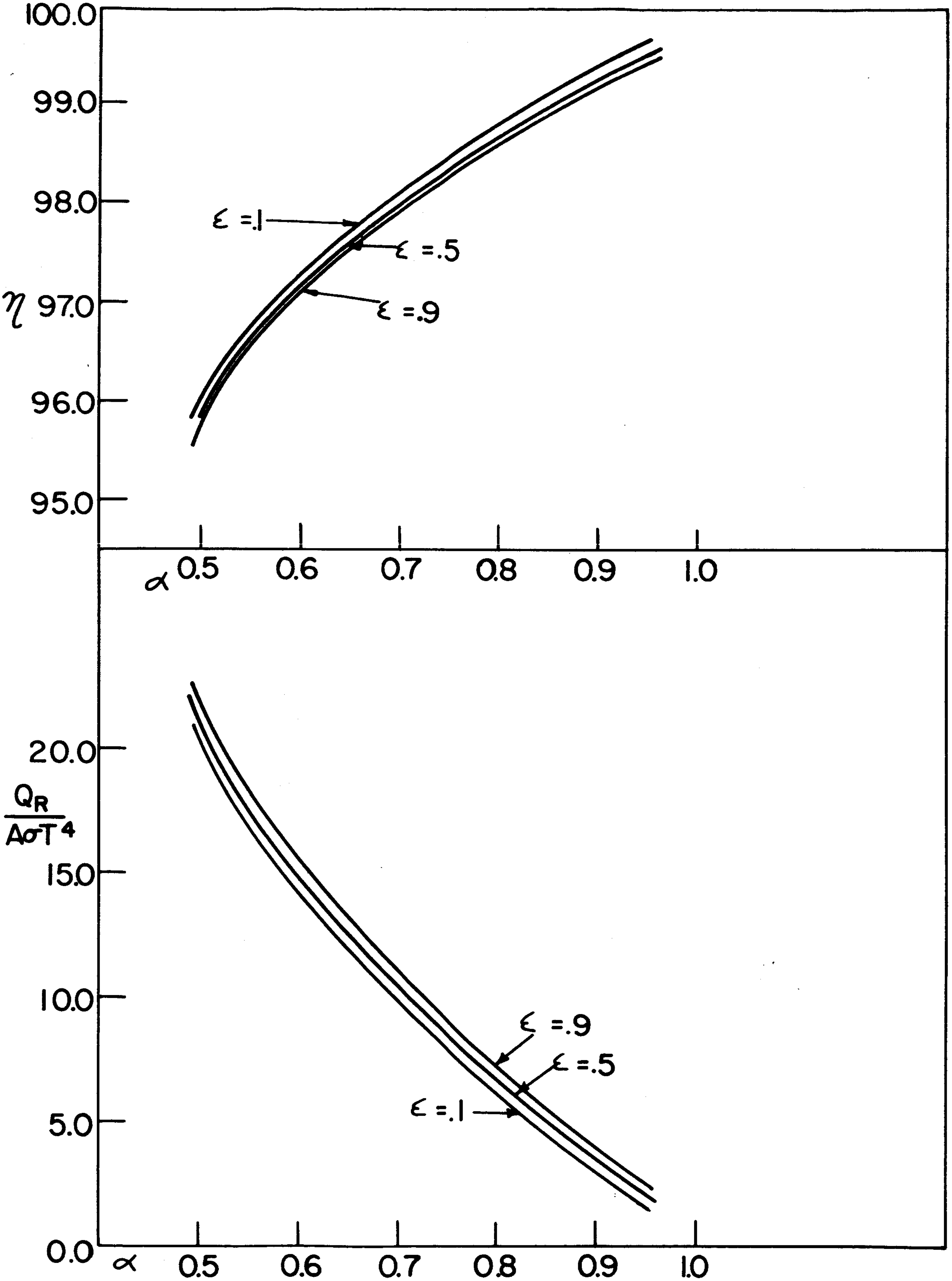

FIG. 9 Cavity Pefformance at T = 1000°K for a 60° perfect paraboloidal reflector. Here Lambert's Law was assumed and reflector radius = 60". Also, ℓ = 4", ℓ/d = 2.5, and R_c = 0.4".

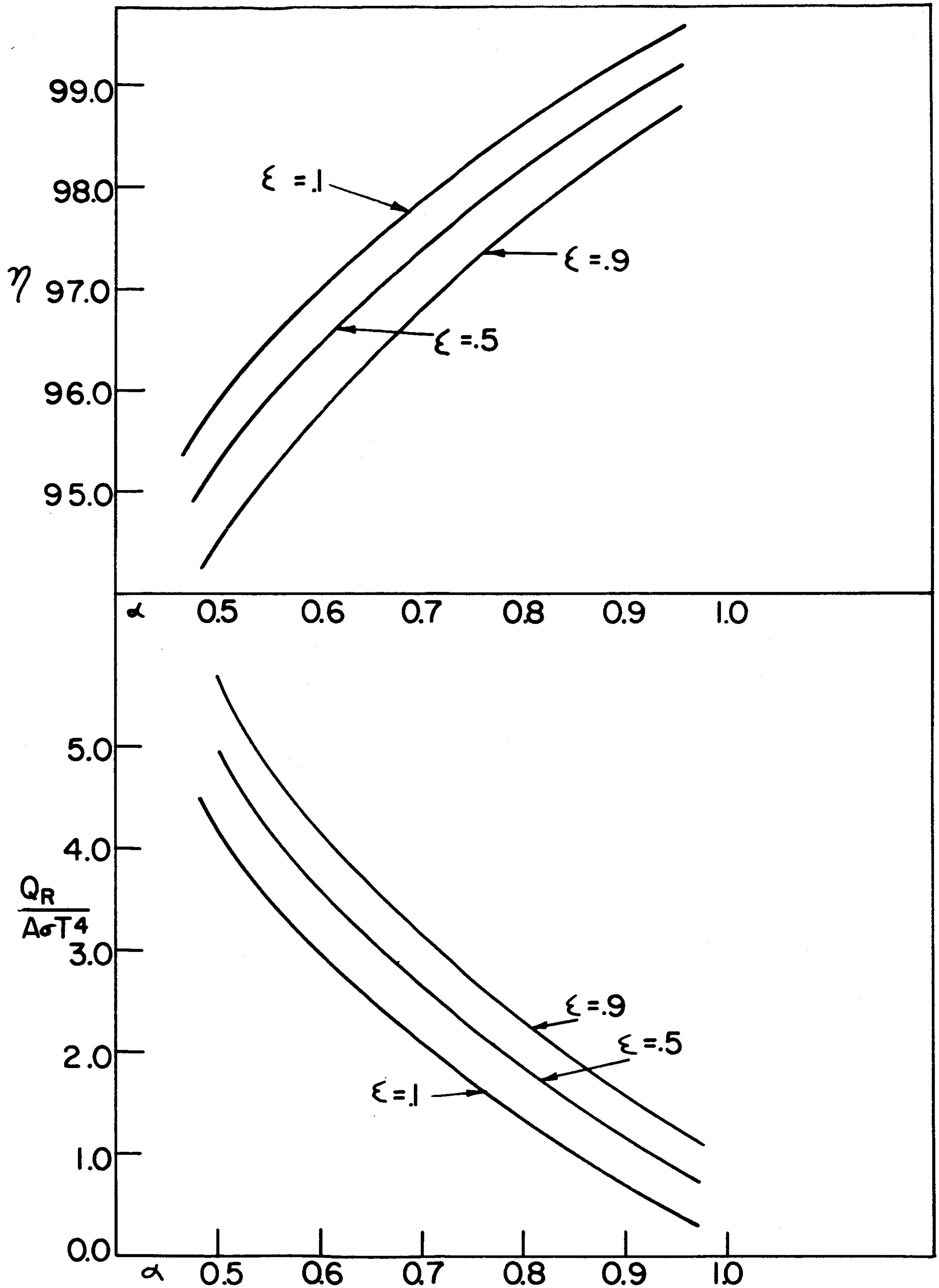

FIG. 10. Cavity performance at T = 1500°K for a 60° perfect paraboloidal reflector. Here Lambert's Law was assumed and reflector radius = 60". Also, ℓ = 4", ℓ/d = 2.5, and R_{-} = 0.4".

Appendix I. Solar Reflectors and Heat Receivers

A mathematical model for analysis of actual solar reflectors has been developed. This model allows one to calculate the energy flux on any arbitrarily shaped focal surface from any arbitrarily shaped reflector surface without making any approximations. Provisions are included for treating random surface errors on the reflector surface, orientation errors of any size, and vignetting* of reflected radiation by a cavity opening. Operative computer programs for evaluating solar reflectors have been developed from these equations. The theoretical details of this model and the descriptions of the resulting computer programs are described in detail in Reference 1.

A detailed mathematical model of a solar collector is a necessary and indispensable tool in any realistic systems study involving solar reflectors. More specifically, it must serve as the starting point for any analytical study of a solar power system involving solar reflectors. Because of the broad scope and generality of this model, its perfection now provides the solar power system designer with tools that have been heretofore unavailable.

This model is currently being used to explore various problem areas concerning solar power systems--specifically systems consisting of solar reflectors and heat receivers (i.e., cavities). This work is limited to be exploratory in nature and will not constitute a detailed systems study on any proposed systems. It is being carried out in order to define clearly the various problem areas and to produce curves that will be representative of the results that one can expect to obtain from actual solar reflector and heat receiver systems.

Lambert's Law

The first problem area under exploration with this model is the interface between the solar collector and the cavity--namely, the cavity opening. The classical directional assumption made for this interface is that this opening can be treated as if it were a plane surface that emitted radiation according to Lambert's law (i.e., the cosine law). Until recently one could calculate the predicted energy flux only on plane surfaces, such as the cavity opening. The radiation passing through this opening was then assumed to obey Lambert's law for any detailed study of the cavity. Clearly this type of approach served to isolate the study and design of the cavity from that of the reflector.

*The term vignetting refers specifically to blockage of reflected light by a cavity opening. This is in contrast to the term blockage which is used to refer specifically to blockage of incident light on the reflector. In addition to vignetting, provisions also exist for treating blockage of incident light.

With the recent perfection of the mathematical model described in Reference 1, it is now possible for the first time to investigate this assumption. This question can be investigated in two ways. First, the actual directional distribution can be calculated. This is best done by looking at a hemispherical cavity located on the principal axis of the reflector with a small opening. Second, the actual energy flux incident on the walls of typical cavities can be calculated and compared with similar results obtained through the use of Lambert's law. This tells how important any deviations from Lambert's law will be for any proposed cavity configuration.

Let

σ_x = circumferential mean deviation of the reflector surface normals

σ_y = radial mean deviation of the reflector surface normals

I = concentration ratio of reflected light. Multiplication of I by the solar constant and the coefficient of reflection results in the actual energy flux/unit area incident on the focal surface point.

Figure 1 shows a sketch of the hemispherical cavity used to determine the directional distribution and the cylindrical cavity used to examine the importance of deviations from Lambert's law for a typical cavity.

For a perfect reflector ($\sigma_x = \sigma_y = 0$) Figure 2 shows a plot of I vs. cos θ for the hemispherical cavity of Figure 1. Figure 3 is a polar plot of these results that clearly shows the directional distribution. Figure 4 shows a plot of I along the walls of the cylindrical cavity. The opening of this cavity was arbitrarily chosen to collect 90% of the reflected energy. Lambert's law has also been plotted in these figures for the purpose of comparison. These results clearly indicate that Lambert's law is invalid for perfect paraboloidal reflectors.

The same results have been obtained for a typical imperfect reflector where $\sigma_x = 5'$, $\sigma_y = 10'$. Figure 5 shows a plot of I vs. cos θ for the same hemispherical cavity; Figure 6 is a polar plot of these results to show the directional distribution; and Figure 7 shows a plot of I for the walls of the cylindrical cavity. Here, also, the opening was arbitrarily chosen to collect 90% of the reflected energy. These results clearly indicate that even for imperfect paraboloidal reflectors Lambert's law is invalid.

The cylindrical cavity results shown in Figures 4 and 7 also indicate that the design of a solar power system on the basis of Lambert's law could lead to significant problems and/or failures. The shift in position and magnitude of the peak of I along the wall of the cylindrical cavity simply cannot be ignored. It must also be pointed out here that these results do not presently take into account blockage of the incident light by the physical structure of the heat receiver; they assume a full paraboloidal reflector with no blockage. The inclusion of such blockage is expected to lead to further deviations from Lambert's law (This is one of the problem areas that will be explored in the near future.).

Cavity Reradiation Losses

The second problem area under exploration is the calculation of the performance of typical heat receivers. A computer program to calculate the performance of cylindrical heat receivers has been developed. The approach used in this work can best be described as an "open cavity" Fredholm integral equation approach. No specific directional distribution has been assumed in this approach; instead, it uses the actual energy flux on the wall of the cavity.

To understand this approach, consider the sketch shown in Figure 8.

Define

x	=	a coordinate specifying a point on the cylindrical cavity
$f(x)$	=	incident energy flux on the wall of the cavity
$T(x)$	=	assumed temperature distribution of the wall of the cavity
σ	=	Stefan-Boltzmann constant
ϵ	=	emissivity of the cavity wall
α	=	absorptivity of the cavity wall
$K(x,x')$	=	kernel of the integral equation. This is a geometrical factor that describes the cavity geometry. It is an infinitesimal area view factor.
$\nu(x)$	=	total energy flux reflected and emitted from the point x of the cavity.

Assuming that the walls of the cavity are diffuse, one obtains

$$\nu(x) = \epsilon \sigma T^4(x) + (1 - \alpha) \left[f(x) + \int_{\substack{\text{walls} \\ \text{of cavity}}} K(x, x') \, \nu(x') \, dx' \right]$$

Here the integral extends over only the material walls of the cavity--hence, the designation "open cavity" approach. The calculation of the kernel $K(x,x')$ for the cylindrical geometry is straightforward and will not be discussed here. The numerical solution of the Fredholm integral equation is carried out by using the well known Liouville-Neumann Series. A temperature distribution $T(x)$ is assumed and this equation is then solved for $\nu(x)$. When $\nu(x)$ is known, the entire performance of the cavity can then be calculated.

Some initial results have been obtained for a perfect 60° paraboloidal reflector (10' diameter) with a cylindrical cavity with a length of 4" and a diameter of 1.6" ($\ell/d = 2.5$). The diameter of the cavity opening was chosen to be 0.8" in order to collect 95% of the reflected energy.

Define

A	=	area of opening
Q_R	=	total energy reradiated out of the cavity opening
η	=	efficiency of the cavity = total energy entering the cavity / total energy conducted through the walls of the cavity.

Figure 9 shows the results obtained for this cavity when it is assumed to be isothermal at 1000°K. Figure 10 shows the same results when this cavity is assumed to be isothermal at 1500°K. In both cases, Lambert's law was assumed for the directional distribution as these results were obtained before the correct distributions were available. These results are presently being obtained with the correct directional distributions.

The results shown in Figures 9 and 10 differ significantly from the usual engineering approach used in the design of solar power systems--namely that the cavity losses can be separated into losses due to multiple diffuse reflections (these are oftentimes neglected) and losses due to reradiation effects from a gray cavity. From the basic integral equation it is clear that this decomposition has no meaning--only the total has a physical meaning; hence it is meaningless to treat multiple diffuse reflection losses as a correction to the gray cavity reradiation losses. The results presented here offer perhaps the first realistic estimates of cavity performance (when the cavity is coupled to a solar reflector). They clearly show the importance of the absorptivity of the material surface of the cavity walls.

All the cavity results obtained to date are for isothermal cavity walls. The use of other temperature distributions is the way that the interface is made between the cavity and the thermal energy storage material and/or the heat exchanger.

Future Plans

Further exploration of the problem areas discussed above will be carried out. Some of these results will be presented at the Sixth AGARD Combustion and Propulsion Colloquium on "Energy Sources and Energy Conversion" at Cannes, France from March 16-20, 1964 and will be published in the proceedings of this conference.

In addition to these problem areas, present plans call for exploration of the following problem areas:

1. A more complete exploration of the Lambertian assumption for various cavities

2. A more complete exploration of typical isothermal cylindrical cavity solutions using the correct directional distribution

3. Exploration of the problem of choosing an optimum cavity opening in order to optimize the power output from specific cavities.

4. Exploration of the effects of blockage of incident light by the physical structure of the heat receiver on the design of solar power systems.

IBM 7094 computer time to perform these studies has been made available by both Allison Div. G.M.C. (Indianapolis, Indiana) and Aerospace Corporation (Los Angeles, California). The results of these studies will be presented in appropriate scientific journals.

Also, at present discussions are under way with various publishers for possible publication of a monograph on the analysis of solar reflectors. As it is envisioned, this book would be about 250 pages in length. The first 100 pages would describe the analysis techniques and would also cover the reduction and use of optical test data to predict solar reflector performance. The last 150 pages would constitute a "design handbook" for solar reflectors. A series of curves would be presented to explore the effects of various parameters (orientation errors, rim angles, surface errors, etc.) on the resulting energy flux distributions. The results presented (approximately 100 hours of IBM 7094 computer time) would be expansive enough to serve as a general guide in the design and specification of solar power systems. They will not, however, answer specific system optimization problems; they will only provide the starting point.

Since the above planned studies will be carried out with existing operative computer programs, it is contemplated that the above research work will be completed with no large expenditure of time required.

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All figures referred to in this appendix are attached between Appendix H. and Appendix I.

PLATES

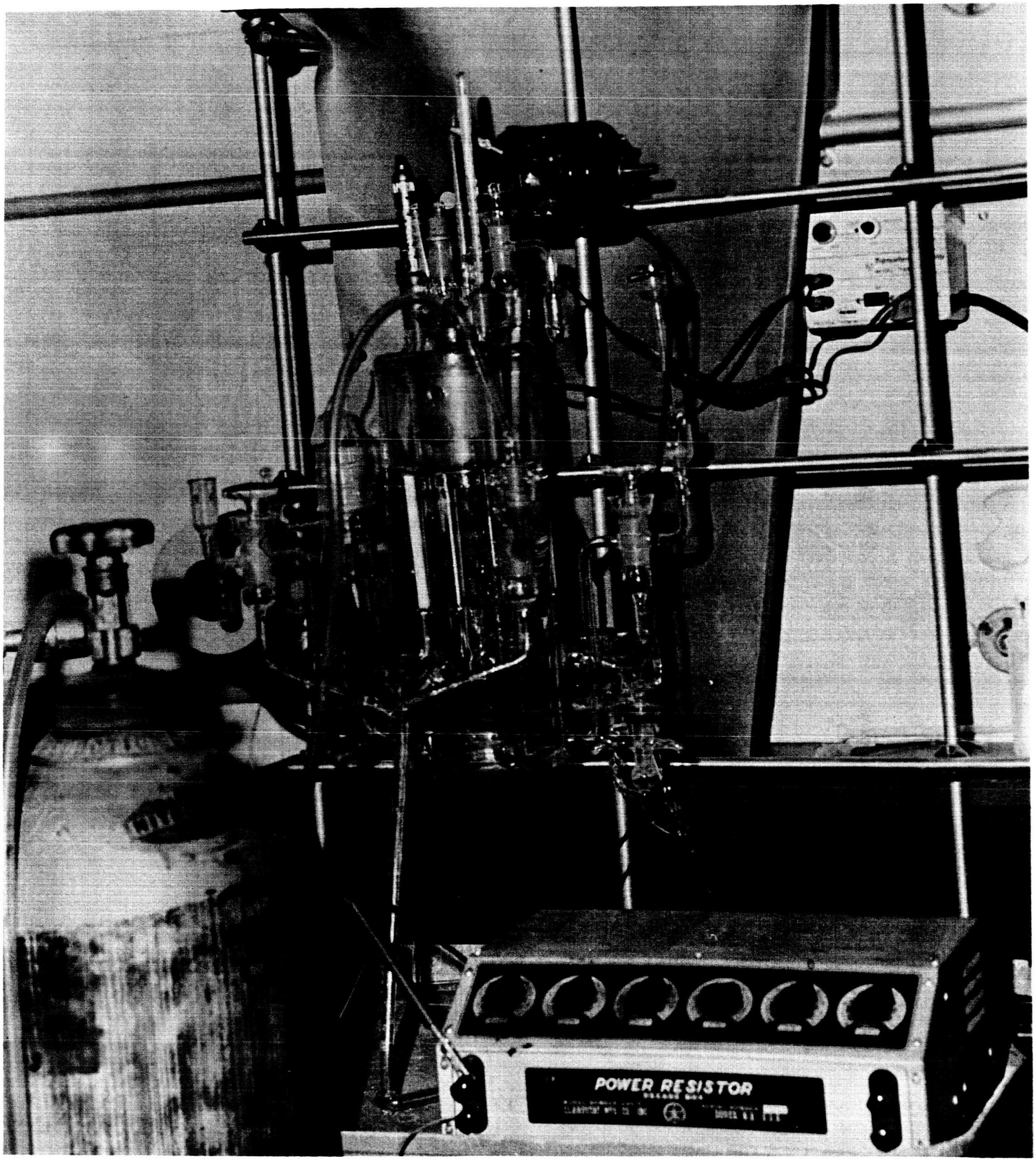

Fig. 1

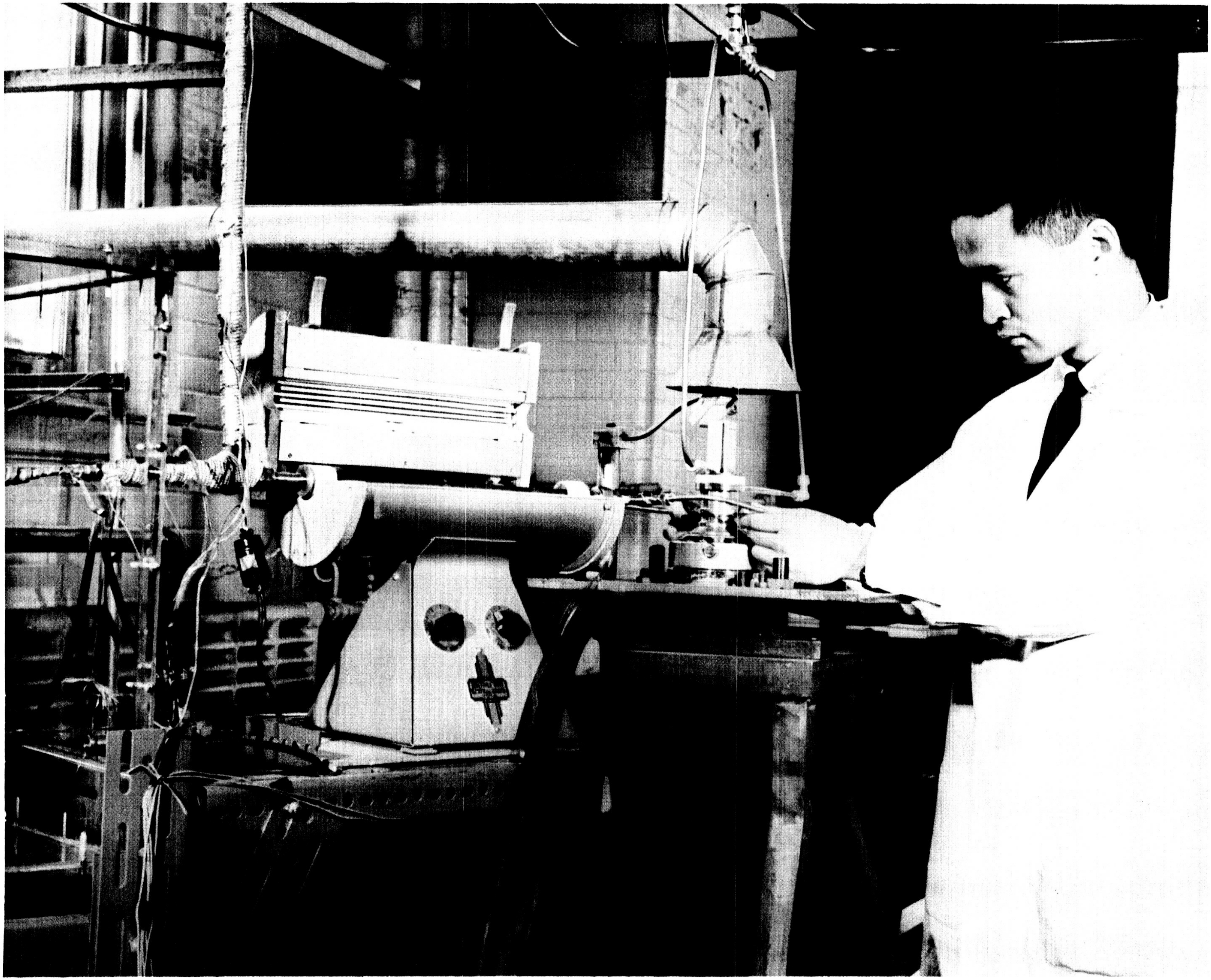

Fig. 2

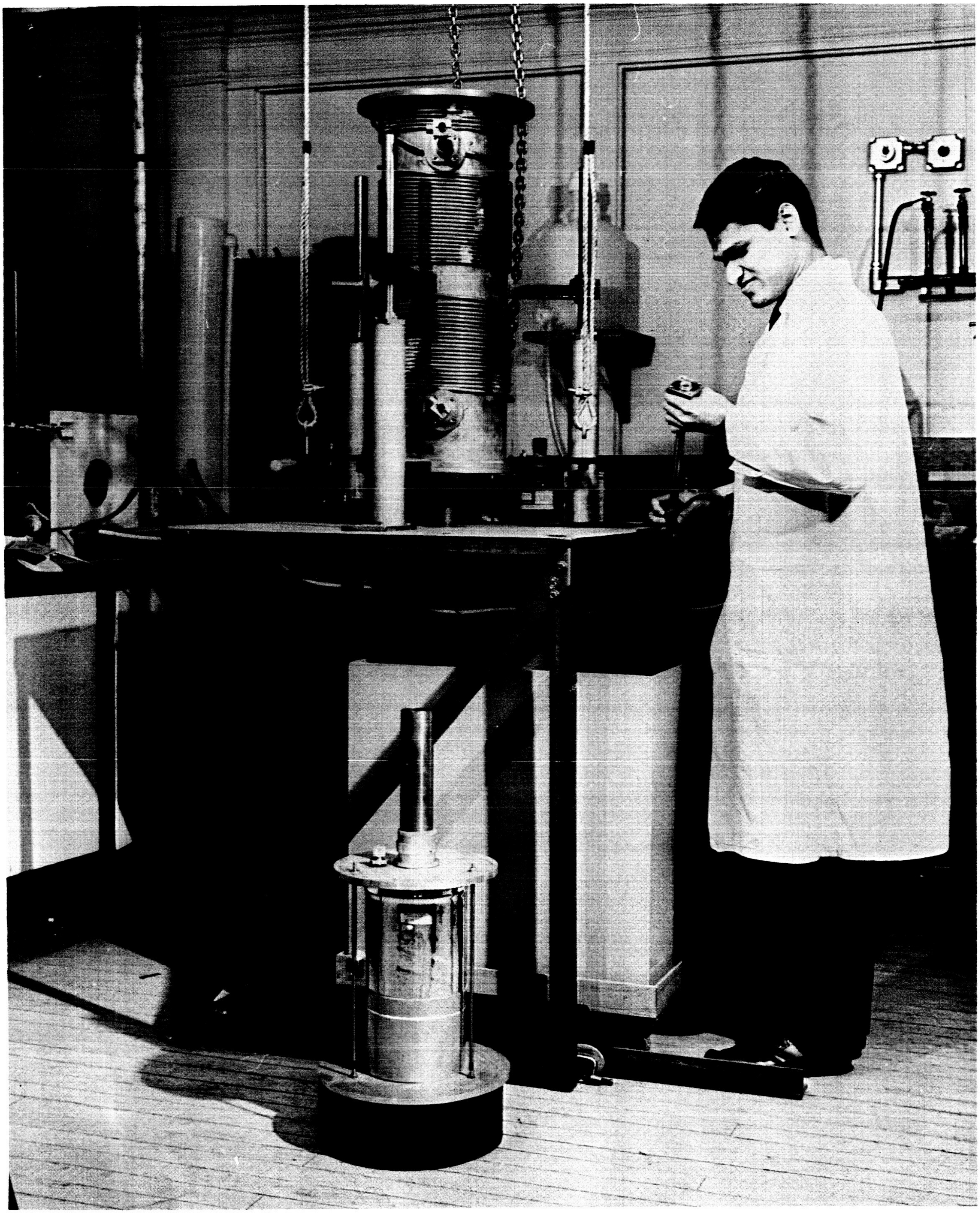

Fig. 3

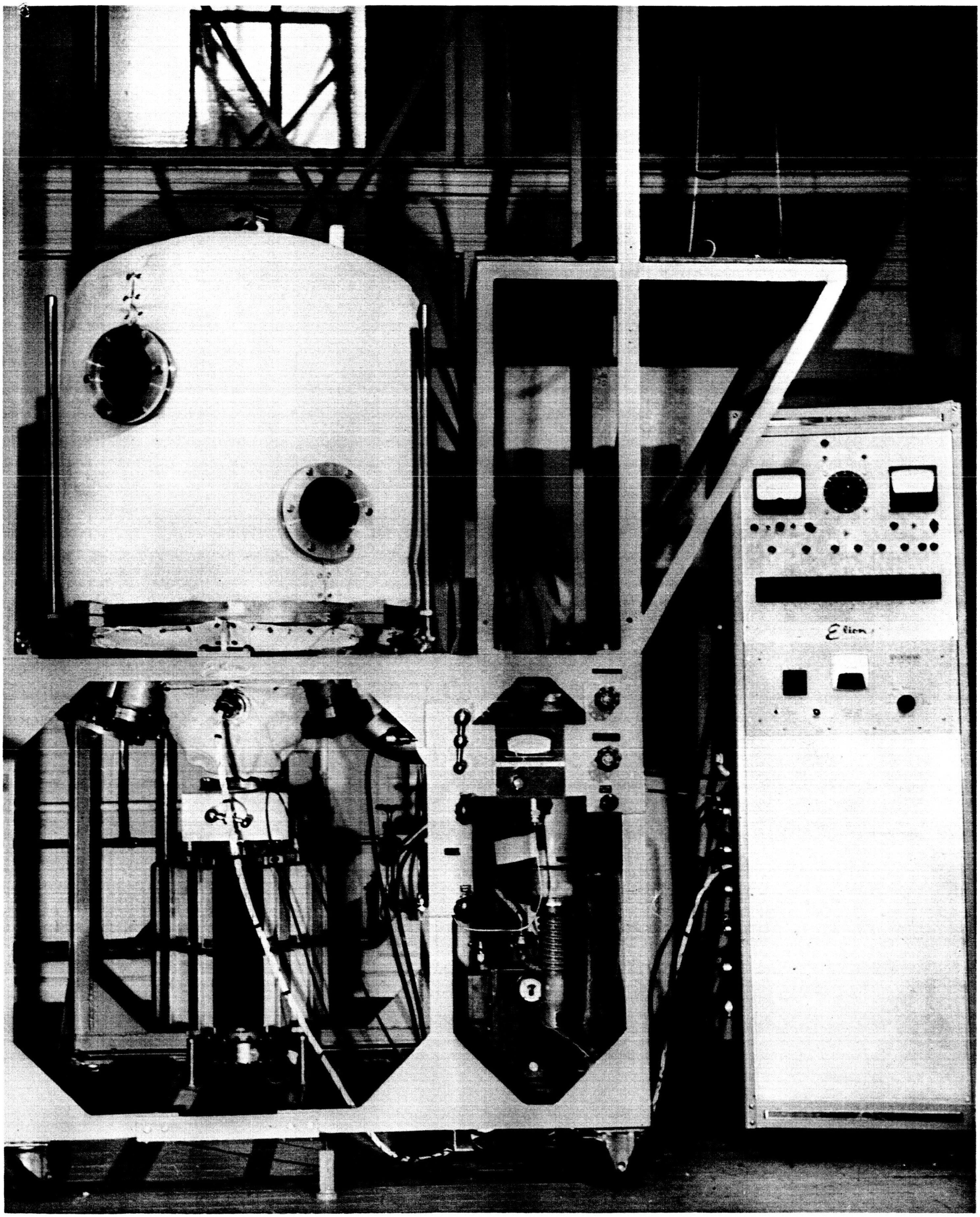

Fig. 4